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THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

1917. Vol. CXII. Part I.

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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen.	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
Acad. Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S.	Agricultural Bulletin of the Federated Malay States.
Agric. Exp. Stat. Univ. Wisconsin Res. Bull.	Agricultural Experimental Station, University of Wisconsin, Research Bulletin.
Agric. Gaz. S. Russia	Agricultural Gazette of Southern Russia.
Agric. J. India	Agricultural Journal of India.
Agric. Ledger	Agricultural Ledger.
Agric. Res. Inst., Pusa Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Agric. and Sylvic	Agriculture and Sylviculture (Petrograd).
Allgem. Brau.-Hopf. Zeit.	Allgemeine Brau- und Hopfen-Zeitung.
Allgem. Gerber-Zeit.	Allgemeine Gerber-Zeitung.
Allgem. Z. Bierbrau. u. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amat. Fotog.	Amator Fotografen.
Amer. Brewers' J.	American Brewers' Journal.
Amer. Brewers' Rev.	American Brewers' Review.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health.
**Amer. J. Sci.*	American Journal of Science.
Amer. Mach.	American Machinist.
Amer. Min.	American Mineralogist.
Amer. Perf.	American Perfumer.
Amer. Phot.	American Photography.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Anal. Soc. Quím. Argentina	Anales de la Sociedad Química Argentina.
Analyst	Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. di Bot.	Annali di Botanica.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Ecole Agric. Montpellier	Annales de l'Ecole nationale d'Agriculture de Montpellier.
Ann. Falsif.	Annales des Falsifications.
Ann. Geol. Min. Russie	Annuaire de la Géologie et de la Minéralogie de Russie.
Ann. hyg. pub. med. legale	Annales d'hygiène publique et de médicine légale.
Ann. Inst. Mines, Petrograd	Annales de l'Institut des Mines, Petrograd.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Inst. Polyt., Petrograd	Annales de l'Institut Polytechnique, Petrograd.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales des Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.

Abbreviated Title.	Journal.
Ann. Soc. Geol. Belg.: Publ. rel. au Congo Belge	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
Apoth. Zeit.	Apotheker-Zeitung.
App. Sci.	Applied Science.
Arb. Gebiet. Physik, Math. Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arb. Gesundh. Amt.	Arbeiten aus dem Gesundheitsamte.
Arch. Anat. Physiol.	Archiv für Anatomie und Physiologie.
Arch. Chem. Mikros.	Archiv Chemie und Mikroskopie.
Arch. Entw.-mech. Org.	Archiv für Entwicklungsmechanik der Organismen.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. farm. sper. sci. aff.	Archivio di farmacologia sperimentale e scienze affini.
Arch. Fisiol.	Archivio di Fisiologia.
Arch. Hyg.	Archiv für Hygiene.
Arch. Int. Med.	The Archives of Internal Medicine.
Arch. ital. Biol.	Archives italiennes de Biologie.
Arch. Med. Pharm. milit.	Archives de Médicine et de Pharmacie militaires.
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
**Arch. Pharm.*	Archiv der Pharmazie.
Arch. physikal. Chem. Glas. Keram.	Archiv für die physikalische Chemie der Glases und der Keramischen Massen.
Arch. Sci. biol. Petrograd	Archives des Sciences biologiques, Petrograd.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned. Indie	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv. Kem. Min. Geol.	Arkiv. för Kemi, Mineralogi och Geologi.
Arm. Beton	Armierter Beton.
**Atti R. Accad. Lincei*	Atti della Reale Accademia dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci.	Atti del Istituto Veneto di Scienze, Ettere ed Arti.
Aust. Pharm. Notes	Australian Pharmaceutical Notes and News.
Beitr. Min. Japan	Beiträge zur Mineralogie von Japan.
Berg. Hüttenm. Rundsch.	Berg- und Hüttenmannisches Rundschau.
**Ber.*	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deuts. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Ber. K. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
Ber. Oberhess. Ges. Natur. Heilkunde.	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Berlin. Klin. Woch.	Berliner Klinische Wochenschrift.
**Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationallen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
**Biochem. J.*	Biochemical Journal.
**Biochem. Zeitsch.*	Biochemische Zeitschrift.
Blätter Zucker.	Blätter für Zuckerrübenbau.
Bd. of Trade J.	Board of Trade Journal.
Bol. Acad. Nac. Ciencias, Cordoba.	Boletín de la Academia Nacíonal des Ciencias, Cordoba.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital.	Bolletino della Società Geologica Italiana.

Abbreviated Title.	Journal.
Boll. Soc. Med.-Chirurg.	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr.	Botanisches Centralblatt.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Brewers' J.	Brewers' Journal.
Brit. and Col. Pharm.	British and Colonial Pharmacist.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Buletinul Chim.	Buletinul Chimie.
Bul. Soc. Romane Stiin.	Buletiuul Societatii Romane de Stiinte.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Petrograd.	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Agric. Intell.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
Bull. Bureau of Standards (U S.A.).	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande.	Bulletin de la Commission Géologique de Finlande.
Bull. Dept. Agric. Ceylon	Bulletin of the Department of Agriculture, Ceylon.
Bull. Dept. Agric. Trinidad	Bulletin of the Department of Agriculture, Trinidad.
Bull. Forest Exp. Stat. Meguro.	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap.	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
Bull. Geol. Inst. Univ. Upsala.	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia.	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Centr. Agric. Exp. Stat. Japan.	Bulletin of the Imperial Central Agricultural Experimental Station of Japan.
Bull. Imp. Inst.	Imperial Institute Bulletin.
Bull. Johns Hopkins Hospital	Bulletin of Johns Hopkins Hospital.
Bull. Ranade Indus. Econ. Inst. Poona.	Bulletin of the Ranade Industrial and Economic Institute, Poona.
Bull. School Mines and Met., Univ. Missouri	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
**Bull. Soc. chim.*	Bulletin de la Société chimique de France.
**Bull. Soc. chim. Belg.*	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim biol.	Bulletin de la Société de chimie biologique.
Bull. Soc. chim. Maurice	Bulletin de la Société chimique de Maurice.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord.	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Ind. Rouen	Bulletin de la Société Industrielle de Rouen.

ABBREVIATED TITLE.	JOURNAL.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J.	Cairo Scientific Journal.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
Canadian Med. Assoc. J.	Canadian Medical Association Journal.
Canadian Mining J.	Canadian Mining Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cement	Cement.
**Centr. Bakt. Par.*	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Kunstdüngerind.	Centralblatt für Kunstdüngerindustrie.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Centr. Zuckerind.	Centralblatt für Zuckerindustrie.
Céramique	Céramique.
Ch. of Comm. J.	Chamber of Commerce Journal.
Chem. App.	Chemische Apparatur.
Chem. Eng.	Chemical Engineer.
Chem. Erde	Chemie der Erde.
Chem. Ind.	Chemische Industrie.
**Chem. News*	Chemical News.
Chem. Trade J.	Chemical Trade Journal.
Chem. Umschau Fett-Ind.	Chemische Umschau über die Fett- und Harz-Industrie.
**Chem. Weekblad*	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zeitsch.	Chemische Zeitschrift.
**Chem. Zentr.*	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
Collegium	Collegium.
**Compt. rend.*	Comptes rendus hebdomadaires des Séances de l'Academie des Sciences.
Compt. rend. l'Acad. d'Agric.	Comptes rendus des Séances de l'Academie d'Agriculture de France.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Carlsberg.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Derm. Woch.	Dermatologische Wochenschrift.
Deut. Essigind.	Deutsche Essigindustrie.
Deut. Mechan. Zeit.	Deutsche Mechaniker Zeitung.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Parfum. Zeit.	Deutsche Parfumerie Zeitung.
Deuts. Zuckerind.	Deutsche Zuckerindustrie.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Electrician	Electrician.
Elektrochem. Zeits.	Elektrochemische Zeitschrift.
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News	Engineering News.
Eng. Rec.	Engineering Record.
Engrais	L'Engrais.
Exper. Stat. Rec.	Experimental Station Record.
Fachl. Mitt. Öst. Tabak.	Fachliche Mitteilungen der Österreichische Tabakregie.
Farber-Zeit.	Färber-Zeitung.

Abbreviated Title.	Journal.
Farben-Zeit.	Farben-Zeitung.
Farm	The Farm (Russia).
Fermentforsch.	Fermentforschung.
Ferrum	Ferrum.
Feuerungstechnik	Feuerungstechnik.
Flora	Flora.
Földtani Közlöny	Földtani Közlöny.
Fühlings Landw. Zeit.	Fühlings Landwirtschaftliche Zeitung.
Gas	Het Gas.
Gas J.	Gas Journal.
Gas Rec.	Gas Record.
**Gazzetta*	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag.	Geological Magazine.
Gerber	Gerber.
Gesundheitsing.	Gesundsheitsingenieur.
Gornosaw. Djelo.	Gornosawodskoje Djelo.
Gummi-Zeit.	Gummi-Zeitung.
Handl. Vijft. Nat.	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Heart	Heart.
Hess. Landw. Zeits.	Hessische Landwirthschaftliche Zeitschrift.
Hyg. Rundsch.	Hygienische Rundschau.
Indian Forest Bull.	Indian Forest Bulletin.
Indian J. Med. Res	Indian Journal of Medical Research.
India-rubber J.	India-rubber Journal.
Ingenieur	De Ingenieur.
Int. Mitt. Bodenk.	Internationale Mitteilungen für Bodenkunde.
Int. Sugar J.	International Sugar Journal.
Int. Z. Metallog.	Internationale Zeitschrift für Metallographie.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Jahrb. K. K. Geol. Reichsanst.	Jahrbuch der K. K. geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur.	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Jernk. Ann.	Jern-kontorets Annaler.
J. d'Agric. prat.	Journal d'Agriculture Pratique.
**J. Agric. Res.*	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. d'Agric. Trop.	Journal d'Agriculture Tropique.
J. Agric. Victoria	Journal of Agriculture, Victoria.
**J. Amer. Chem. Soc.*	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
**J. Biol. Chem.*	Journal of Biological Chemistry, New York.
J. Board Agric.	Journal of the Board of Agriculture.

ABBREVIATED TITLE.	JOURNAL.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo	*See* Kōgyō- Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chim. physique	Journal de Chimie physique.
J. Coll. Agric. Sapporo	Journal of the College of Agriculture, Sapporo, Japan.
J. Coll. Agric. Tohoku	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
J. Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
**J. Coll. Sci. Tokyo*	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung.
J. Genetics	Journal of Genetics.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Imp. Gas Assoc. Tokyo	Journal of the Imperial Gas Association of Tokyo.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Petroleum Tech.	Journal of the Institute of Petroleum Technologists.
J. Inst. Sanit. Eng.	Journal of the Institute of Sanitary Engineers.
J. Landw.	Journal für Landwirtschaft.
J. Manchester School Tech.	Journal of the Manchester School of Technology.
J. Marine Biol. Assoc. U.K.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Expt. Ther.	Journal of Pharmacology and Experimental Therapeutics.
**J. Physical Chem.*	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
**J. pr. Chem.*	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Soc. New South Wales.	Journal and Proceedings of the Royal Society of New South Wales.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
**J. Russ. Phys. Chem. Soc.*	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Russe Métall.	Journal de la Société Russe de Métallurgie.
J. Textile Inst.	Journal of the Textile Institute.
J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
K. Svenska Vet.-Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.

ABBREVIATED TITLE.	JOURNAL.
Kali	Kali.
Karbid u. Azet. . . .	Karbid und Azetylen.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . .	Keramisch Rundschau.
Kew Bull. . . .	Kew Bulletin.
Kiserlet Közl. . . .	Kiserlet Közlémények.
Klein u. Mittelbrauer . .	Klein und Mittelbrauer.
Kongl. Landtbr. Handl. Tidskr.	*See* Bull. Agric. Intell.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
**Kolloid Zeitsch.* . .	Kolloid Zeitschrift.
**Koll. Chem. Beihefte* .	Kolloid-chemische Beihefte.
Kosmos	Kosmos (Lemberg).
Kühn-Archiv . . .	Kühn-Archiv.
Kunststoffe . . .	Kunststoffe.
Lancet	The Lancet.
Landw. Jahrb. . . .	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat. .	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev. . .	Leather Trades Review.
Leather Trades Year Boo .	Leather Trades Year Book.
Leather World . . .	Leather World.
Ledertech. Rundsch. . .	Ledertechnische Rundschau.
Leipzig. Monatsch. Textil-Ind.	Leipziger Monatschrift für Textil-Industrie
Le Radium . . .	Le Radium.
L'Ind. Chimica . . .	L'Industria Chimica.
L'Ind. Chimique . . .	L'Industrie Chimique.
Lilly Sci. Bull. . . .	Lilly Scientific Bulletin.
Local Govt. Bd. Reports .	Local Government Board Reports.
Louisiana Bull. . . .	Louisiana Bulletin.
Louisana Planter . .	Louisiana Planter.
Lunds. Univ. Arsskr. . .	Lunds Universitets Års-skrift.
Math. és Termés. Ért. .	Mathematikai és Természettudományi Értesitö, Budapest.
Mat. Grasses	Les Matières Grasses.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland . .	Meddelser on Grönland.
Med. Chron. . . .	Medical Chronicle.
Med. Klinik . . .	Medizinesche Klinik.
Mem. Acad. Sci. Petrograd.	Mémoires de l'Académie Impériale des Sciences de Petrograd.
Mem. Accad. Lincei . .	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō .	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres et Salpêtres .	Mémoriale des Poudres et Salpêtres.
Mem. Soc. Ing. Civ. . .	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Natur. Kiev .	Mémoires de la Société des Naturalistes de Kiev.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz . . .	Metall und Erz.
Met. and Chem. Eng. .	Metallurgical and Chemical Engineering.
Metallurgie . . .	Metallurgie.

Abbreviated Title.	Journal.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. and Eng. Rev.	Mining and Engineering Review.
Ministry of Agric. Egypt. Tech. Sci. Service	Ministry of Agriculture of Egypt. Technical Science Service.
Mitt. Centralst. wiss.-techn. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen.
Mitt. deut. Landw.-Ges.	Mittheilungen der deutschen Landwirthschafts-Gesellschaft.
Mitt. deut. milchwirt. Ver.	Mitteilungen des deutschen milchwirtschaftlichen Vereins.
Mitt. geol. Landesanst.	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. k. k. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle.	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Molk.-Zeit.	Molkerei-Zeitung.
**Monatsh.*	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
**Mon. Sci.*	Moniteur Scientifique.
Montan. Rundsch.	Montanische Rundschau.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Mycol. Zentr.	Mycologisches Zentralblatt.
Nachr. Ges. Wiss. Göttingen.	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rdsch.	Naturwissenschaftliche Rundschau.
Nephthanoje Djelo	Nephthanoje Djelo.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oelmotor	Der Oelmotor.
Oesterr. Chem.-Zeit.	Oesterreichische Chemiker-Zeitung.
Oesterr. Z. Berg- u. Hüttenw.	Oesterreichische Zeitschrift fürBerg- und Hüttenwesen.
Oil and Colour Trades J.	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep.	Oil, Paint, and Drug Reporter.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
Pahasapa Quart.	Pahasapa Quarterly.
Paper	Paper.
Paper Maker	Paper Maker.
Paper Making	Paper Making.
Papierfabr.	Papier-Fabrikant.
Papier-Zeit.	Papier-Zeitung.

ABBREVIATED TITLE.	JOURNAL.
Perf. and Essent. Oil Rec. .	Perfumery and Essential Oil Record.
Per. spis. Sofia . . .	Periodicesko spisanie Sofia.
Petroleum	Petroleum.
Pflüger's Archiv . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Post. . . .	Pharmazeutische Post.
Pharm. Weekblad . .	Pharmaceutisch Weekblad.
Pharm. Zeit. . . .	Pharmazeutische Zeitung.
Pharm. Zentr.-h. . .	Pharmazeutische Zentralhalle.
Pharmazevt. J. . . .	Pharmazevtizeski Journal.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . .	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci. . .	Philippine Journal of Science.
Phot. Ind.. . . .	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr. . . .	Photographische Korrespondenz.
Phot. Rundsch. . . .	Photographische Rundschau.
Physical Rev. . . .	Physical Review.
Physikal. Zeitsch. . .	Physikalische Zeitschrift.
Porto Rico Exper. Stat. Bull.	Porto Rico Experiment Station Bulletin.
Proc. Amer. Phil. Soc. .	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc. .	Proceedings of the American Physiological Society.
**Proc. Amer. Soc. Biol. Chem.*	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Amer. Wood Preservers' Assoc.	Proceedings of American Wood Preservers' Association.
Proc. Austral. Inst. Min. Eng.	Proceedings of the Australasian Institute of Mining Engineers.
Proc. Brit. Foundrymen's Assoc.	Proceedings of British Foundrymen's Association.
Proc. Camb. Phil. Soc. .	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc. .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. .	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng. . .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. .	Proceedings of the Institution of Mechanical Engineers.
Proc. Inst. Min. and Met. .	Proceedings of the Institution of Mining and Metallurgy.
**Proc. K. Akad. Wetensch. Amsterdam.*	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci. .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow .	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. London .	Proceedings of the Physical Society of London.
Proc. Physiol. Soc. . .	Proceedings of the Physiological Society.
Proc. Roy. Irish Acad. .	Proceedings of the Royal Irish Academy.
**Proc. Roy. Soc.* . . .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. . .	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med. . .	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland .	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania .	Proceedings of the Royal Society of Tasmania.
Proc. Soc. Chem. Ind. Victoria.	Proceedings of the Society of Chemical Industry, Victoria.

ABBREVIATED TITLE.	JOURNAL.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Queensland Agric. J.	Queensland Agricultural Journal.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Nécrland.	Recueil des travaux botaniques Néerlandaises.
**Rec. trav. chim.*	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
Rend. Soc. Chim. Ital.	Rendiconto della Società Chimica Italiana.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Rep. Pharm.	Repertoire de Pharmacie.
Rev. Viticolt	Revista Viticolt.
Rev. gén. Bot.	Revue générale de Botanique.
Rev. gén. Chim. pure appl.	Revue générale de Chimie pure et appliquée.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid.	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
Riv. Min. Crist. Ital.	Rivista di Mineralogia e Cristallografia Italiana.
Russian Mining J.	Russian Mining Journal.
Sbornik Klubu Pri.	Sbornik Klubu Prirodovedeckeho (Prague).
Schimmel's Rep.	Schimmel's Reports.
Schweiz. Apoth. Zeit.	Schweizerische Apotheker Zeitung.
Schweiz. Woch. Chem. Pharm.	Schweizerische Wochenschrift für Chemie und Pharmacie.
Science	Science.
Scient. Amer.	Scientific American.
**Sci. Ind. Rep. Roure-Bertrand Fils.*	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tohoku Imp. Univ.	Science Reports, Tohoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifenfabr.	Der Seifenfabrikant.
Seifensied. Zeit.	Seifensieder Zeitung.
Selsk. Khoz. Les. Petrograd	Selskoie Khoziaistvo i Lesovodstvo Petrograd.
Shoe and Leather Rep.	Shoe and Leather Reporter.
Silikat-Zeits.	Silikat-Zeitschrift.
Sitzungsber. Ges. Naturwiss. Marburg.	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. K. Akad. Wiss. Wien.	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
Sitzungsber. Med. Naturwiss. Ges. Münster.	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.

ABBREVIATED TITLE.	JOURNAL.
Sitzungsber. Naturforsch. Ges. Petrograd.	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
Sitzungsber. Naturforsch. Ges. Rostock.	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen.	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll.	Smithsonian Miscellaneous Collections.
Soil Sci.	Soil Science.
South African J. Sci.	South African Journal of Science.
Spezialmonats. Brau- Malz.	Spezialmonatshefte für Brau- und Malzerei betriebskontrolle.
Sprechsaal.	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Strahlenther.	Strahlentherapie.
Sucr. Indig.	Sucrerie Indigène.
Süddeut. Apoth. Zeit.	Süddeutsche Apotheker Zeitung.
Suikerind.	De Suikerindustrie.
Suom. Tied. Toim.	Suomalaisen Tiedeakatemian Toimituskia.
Svensk Kem. Tidskr.	Svenska Kemisk Tidskrift.
T.	Transactions of the Chemical Society.
Teknikern	Teknikern.
Tekn. Tidsk.	Teknisk Tidskrift.
Textile Col.	Textile Colourist.
Ther. Gegenw.	Die Therapie der Gegenwart.
Ther. Monatsh.	Therapeutische Monatshefte.
Tidsk. Kemi, Farm., Ter.	Tidskrift Kemi, Farm. og Terape.
Tidsk. Teknikern.	Tidskriften Teknikern.
Times Eng. Supplt.	Times Engineering Supplement.
Tonind.-Zeit.	Tonindustrie-Zeitung.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Foundrymen's Assoc.	Transactions of the American Foundrymen's Association.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Engl. Ceram. Soc.	Transactions of the English Ceramic Society.
* *Trans. Faraday Soc.*	Transactions of the Faraday Society.
Trans. Inst. Metals	Transactions of the Institute of Metals.
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Surveyors' Inst.	Transactions of the Surveyors' Institute.
Trav. Mus. Geol. Acad. Sci. Petrograd.	Travaux de Musée Geologique près l'Academie Impériale des Sciences de Petrograd.
Trav. Soc. Natur. Petrograd.	Travaux de la Société Impériale des Naturalistes de Petrograd.
Tropenpflanzer.	Tropenpflanzer.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.

ABBREVIATED TITLE.	JOURNAL.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind.	United States Bureau of Plant Industry.
U.S. Comm. Rept.	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull.	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Ver. deut. Textilver.	Verein deutscher Textilveredlungsindustrie.
Verh. Geol. Reichsanst. Wien.	Verhandlungen der k. k. geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlung der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl.	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Verslag Landb.	Verslag Landbouwkund Onderzoek Ryklandbouwproefstat.
Vet. Rec.	Veterinary Record.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin
Videnskab. Skrifter	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wasser u. Gas	Wasser und Gas.
West Ind. Agric. News	West Indian Agricultural News.
West Ind. Bull.	West Indian Bulletin.
Westnik Sacch. Prom.	Westnik Saccharnoi Promyschlenosti.
Wiener Klin. Woch.	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wochbl. Papierfabr.	Wochenblatt für Papierfabrikation.
Woch. f. Brau.	Wochenschrift für Brauerei.
Yakugakuzashi	Yakugakuzashi.
Zeitsch. allg. Physiol.	Zeitschrift für allgemeine Physiologie.
**Zeitsch. anal. Chem.*	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
**Zeitsch anorg. Chem.*	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
**Zeitsch. Elektrochem.*	Zeitschrift für Elektrochemie.
Zeitsch. exp. Path. Ther.	Zeitschrift für experimentelle Pathologie und Therapie.
Z. Farben-Ind.	Zeitschrift für Farben-Industrie.
Z. Forst- u. Jagdwesen	Zeitschrift für Forst- und Jagdwesen.
Z. Gärungsphysiol.	Zeitschrift für Gärungsphysiologie.
Z. ges. Brauw.	Zeitschrift für das gesammte Brauwesen.
Zeitsch. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Zeitsch. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Zeitsch. Immunit.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Zeitsch. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Kali	Zeitschrift für Kali.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.

ABBREVIATED TITLE.	JOURNAL.
Z. landw. Versuchsw. Oesterr.	Zeitschrift für das landwirtschaftlichen Versuchswesen in Oesterreich.
Z. öffentl. Chem. . .	Zeitschrift für öffentliche Chemie.
**Zeitsch. physikal. Chem.* .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre.
Zeitsch. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol. . .	Zeitschrift für praktische Geologie.
Z. Spiritusind. . . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Mikrosk. .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
**Zeitsch. wiss. Photochem.* .	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuckerind. Böhm.. .	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Trimethylene [αγ-Propylene] Oxide. I. Preparation and Characterisation. C. G. DERICK and D. W. BISSELL (*J. Amer. Chem. Soc.*, 1916, **38**, 2478—2486).—The authors consider that the αγ-propylene oxide prepared and described by Reboul (A., 1879, 127) was very impure, and as the method of preparation only gave a 5% yield, they have devised a new method of preparing the oxide. γ-Chloropropyl acetate (75 grams) is added drop by drop to a mixture of potassium hydroxide (150 grams) and water (12 c.c.) at 100° with continual shaking. Along with αγ-propylene oxide some allyl alcohol and allyl chloride are obtained. These unsaturated compounds are removed from the crude distillate by the addition of bromine to the mixture immersed in ice, followed by subsequent distillation. The αγ-propylene oxide so obtained (yield, 22·5%) is a colourless, pleasant smelling, aromatic liquid, completely miscible with water, b. p. 47·8°/760 mm. (corr.), D_4^{25} 0·8930; n^{24} 1·3897. Bromine only attacks it very slowly, on long contact. A violent reaction occurs when phosphorus pentachloride is added to it, αγ-dichloropropane being formed. The oxide reacts with Grignard reagents to give the higher alcohols, hexan-α-ol being prepared in this way. With acetyl chloride, a vigorous action occurs, γ-chloropropyl acetate being regenerated. With ferric chloride solution, αγ-propylene oxide gives a brown precipitate. W. G.

Esters of Telluric Acid. G. Pellini (*Gazzetta*, 1916, **46**, ii 247—250).—These esters cannot be prepared by the usual methods but the *methyl* ester, $Te(OMe)_6$, is readily obtained in white, shin ing laminæ, m. p. 85—87° (corr., with previous softening), by gradual addition of finely powdered, dry telluric acid to a solution of diazomethane in absolute ether. It has a faint, irritant odour which becomes more acute when its aqueous solution is heated, and it is readily hydrolysed by water, dilute hydrochloric acid, or dilute alkali hydroxide solution. The composition of this ester furnishes fresh confirmation of the constitution of telluric acid, $Te(OH)_6$, and of the sexavalency of tellurium. T. H. P.

Manufacture of Esters. G. Boiteau (Fr. Pat., 478435; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—A mixture of an ester of ethylene glycol and an alcohol is heated, preferably in the presence of a small quantity of a catalyst, such as sulphuric acid. Acetaldehyde is evolved, and the corresponding ester of the alcohol is contained in the residue. The process is of general applicability, being obtained with primary, secondary, and tertiary alcohols and with aromatic hydroxy-compounds. H. W.

The Constitution of the Phosphoric Esters of Glycerol. O. Bailly (*Ann. Chim.*, 1916, [ix], **6**, 96—154, 215—278).—A résumé of work already published (compare A., 1915, i, 73, 211, 371, 492; 1916, i, 113). W. G.

Preparation of Acetic Acid and Acetaldehyde from Acetylene. H. Dreyfus (Fr. Pat., 479656; from *J. Soc. Chem. Ind.*, 1916, **35**, 1179).—In the preparation of acetaldehyde by the combination of water with acetylene in the presence of a mercury salt, a liquid medium is employed in which the latter is soluble (for example, acetic acid) or which has a greater solvent power for acetylene than water (for example, acetone). In order to convert the acetaldehyde into acetic acid, oxidising substances are added, such as hydrogen peroxide, perborates, percarbonates, permanganates, dichromates, ozone, etc., or the oxidation may be effected by oxygen or air, with or without catalysts, such as cerium oxide, vanadium pentoxide, cerium salts, copper acetate, manganates, manganese or copper nitrate, platinum or palladium sponge, etc. Thus, acetylene (130 parts) and oxygen (80—100 parts) are passed into a mixture of glacial acetic acid (400 parts), water (100 parts), mercuric nitrate (50 parts), and cerium oxide (10 parts) at 50—100°. Acetic acid is produced continuously, and may be drawn off at intervals and distilled, the residue being returned to the reaction vessel. H. W.

Preparation of Anhydrides of Aliphatic Acids. H. Dreyfus (Fr. Pat., 478951; from *J. Soc. Chem. Ind.*, 1916, **35**, 1179).—Anhydrides of aliphatic acids may be prepared by distilling a dry, intimate mixture of a pyrosulphate with a salt of the appropriate acid; thus acetic anhydride is obtained from sodium acetate and sodium pyrosulphate. Diluents such as acetic anhydride or acetic acid may be employed. H. W.

Oxidation of Branched Chain Fatty Acids. I. Action of Hydrogen Peroxide on the Homologues of *iso*Butyric Acid. P. A. LEVENE and C. H. ALLEN (*J. Biol. Chem.*, 1916, **27**, 433—462).—The oxidation of the higher homologues of *iso*butyric acid of the general formula $CHMe_2\cdot[CH_2]_n\cdot CH_2\cdot CH_2\cdot CO_2H$ by means of hydrogen peroxide yields three products:

$$CHMe_2\cdot[CH_2]_n\cdot CH_2\cdot CHO,$$

$CHMe_2\cdot[CH_2]_n\cdot COMe$, and acetone. The reaction proceeds most favourably when the solution of the organic acid is slightly acid and when an amount of peroxide solution equivalent to $3\frac{1}{2}$ atoms of oxygen is employed for the reaction. Under these conditions, acetone is the predominating product and is identified by its *p*-nitrophenylhydrazine derivative. The aldehydes resulting from the oxidation in the α-position are identified by further oxidation to the corresponding acids.

The yield of acetone usually diminishes as the distance between the tertiary carbon atom and the carboxyl group becomes greater. A marked exception occurs in the case of *iso*valeric acid, which yields more acetone than *iso*butyric acid.

The acids required for the investigation are prepared according to the following set of reactions: $R\cdot CH_2\cdot OH \longrightarrow R\cdot CH_2I \longrightarrow R\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow R\cdot CH(CO_2H)_2 \longrightarrow R\cdot CH_2\cdot CO_2H$. The higher acid thus obtained is converted into the corresponding alcohol, $R\cdot CH_2\cdot CO_2H \longrightarrow R\cdot CH_2\cdot CO_2Et \longrightarrow R\cdot CH_2\cdot CH_2\cdot OH$, which then forms the starting point for the preparation of the next higher homologous acid.

*iso*Amyl alcohol is purified by means of its barium compound, and the corresponding iodide, after condensation in the usual way with malonic ester, is transformed into δ-methylhexoic acid boiling at 216°/762 mm., which is rather higher than the values previously recorded. The ethyl ester has b. p. 182·7° (corr.)/750 mm., and the *amide*, $C_7H_{15}ON$, m. p. 103·5—104° (corr.). The reduction of the ester to the corresponding alcohol is effected by sodium, which is suspended in boiling toluene and divided into a fine emulsion by vigorous stirring. The yield of alcohol amounts to 60—65% of the theory, calculated on the basis of the ester used, or to 90—95% if the recovered acid is taken into consideration.

ϵ-*Methylhexyl alcohol*, $C_7H_{16}O$, has b. p. 170·5° (corr.)/755 mm., D^{25} 0·8192; *phenylurethane*, $C_{14}H_{21}O_2N$, m. p. 82·5° (corr.); *iodide*, b. p. 195—195·2° (corr.)/765 mm. By condensation of the iodide with malonic ester and subsequent hydrolysis, α-*carboxy*-ζ-*methyloctoic acid*, $C_{10}H_{18}O_4$, is formed, m. p. 100—100·3° (corr.), *ethyl* ester, b. p. 155° (corr.)/15 mm., which is then converted into ζ-*methyloctoic acid*, $C_9H_{18}O_2$, b. p. 248°/765 mm., or 140·5°/15 mm. (corr.); *amide*, m. p. 106·5° (corr.); *ethyl* ester, b. p. 220·5° (corr.)/764 mm. Subsequent treatment with sodium in the manner already indicated leads to the formation of η-*methyloctyl alcohol*, b. p. 206° (corr.)/761 mm., D^{25} 0·8260; *phenylurethane*, m. p. 66·4° (corr.); *iodide*, b. p. 120° (corr.)/20 mm.

The following compounds have been similarly prepared: α-*carboxy*-θ-*methyldecoic acid*, $C_{12}H_{22}O_4$, m. p. 92° (corr.); *ethyl* ester,

b. p. 182° (corr.)/18 mm.; *θ-methyldecoic acid*, $C_{11}H_{22}O_2$, b. p. 174—174·5° (corr.)/23 mm.

Starting from *iso*butyl alcohol, the corresponding compounds have been obtained with the following constants: *γ-methylpentoic acid*, b. p. 199·2—199·7°; δ-methylamyl alcohol, b. p. 153°/760 mm.; *phenylurethane*, m. p. 48° (corr.); *iodide*, b. p. 173·2° (corr.)/762 mm.; *α-carboxy-ε-methylheptoic acid*, $C_9H_{16}O_4$, m. p. 86·5° (corr.); *ε-methylheptoic acid*, $C_8H_{16}O_2$, b. p. 126—127° (corr.)/14 mm. and 232° (corr.)/762 mm., *amide*, glistening plates, m. p. 114° (corr.), *ethyl* ester, b. p. 200·3° (corr.)/761 mm.; *ζ-methylheptyl alcohol*, b. p. 188·5° (corr.)/764 mm., D^{25} 0·8230, *phenylurethane*, m. p. 81—81·4° (corr.), *iodide*, b. p. 100° (corr.)/17 mm.; *α-carboxy-η-methylnonoic acid*, m. p. 89·5—90° (corr.); and *η-methylnonoic acid*, $C_{10}H_{20}O_2$, b. p. 155·6° (corr.)/16 mm.

After treatment of the above branched chain fatty acids with hydrogen peroxide, the presence of the higher ketones is demonstrated by an indirect method; the amount of the mixed ketones is estimated, and from this is deducted the amount of acetone present in the same solution. The higher ketones are not isolated in the pure condition. H. W. B.

Lithofellic Acid. HANS FISCHER (*Ber.*, 1916, **49**, 2413—2415. Compare A., 1915, i, 214).—Lithofellic acid changes into an oily lactone on treatment with hydrochloric acid and alcohol, and this yields *deoxylithofellenic acid*, $C_{20}H_{34}O_3$, m. p. 174—175°, on hydrolysis with barium hydroxide. The same lactone and unsaturated acid were described by Jünger and Klages (A., 1896, i; 194), but they gave the latter the formula $C_{18}H_{30}O_3$, and m. p. 152°.

A re-examination of lithofellic acid confirms the old formula, $C_{20}H_{36}O_4$. The author therefore abandons his idea that the acid is a hydrogenated cholic acid or a bile acid of any kind, and now believes that it originates in the fodder of the cattle, possibly in the pods of the South American *Prosopys*. J. C. W.

Action of Oxalyl Chloride on Primary, Secondary, and Tertiary Alcohols. ROGER ADAMS and L. F. WEEKS (*J. Amer. Chem. Soc.*, 1916, **38**, 2514—2519).—All the primary alcohols examined immediately reacted with oxalyl chloride at the ordinary temperature, giving simple esters (compare Staudinger, A., 1913, i, 604, 606). Three secondary alcohols were examined, and of these benzhydrol gave a small yield of benzhydryl ether, whilst phenylmethylcarbinol and menthol gave as principal products the corresponding unsaturated compounds, styrene and menthene. The three tertiary alcohols, trimethylcarbinol, dimethylethylcarbinol, and triphenylcarbinol, all yielded chlorides and oxalic acid, but pinacone yielded pinacolin and pinacone carbonate, the oxalyl chloride acting in this case like carbonyl chloride.

W. G.

The Crystallisation of Calcium Tartrate. F. D. CHATTAWAY (*J. Amer. Chem. Soc.*, 1916, **38**, 2519—2522).—When a soluble

calcium salt is added to a neutral solution of a soluble tartrate, it is the *hexahydrate*, $C_4H_4O_6Ca,6H_2O$, which first separates in felted masses of needles. This form is, however, unstable at the ordinary temperature, and is transformed rapidly into the orthorhombic tetrahydrate. This change is facilitated by rise in temperature or by stirring the precipitate. W. G.

The Molecular Weight of some Alcoholates of Chloral and Butylchloral in Benzene Solution. MARGUERITE WILLCOX and ROGER F. BRUNEL (*J. Amer. Chem. Soc.*, 1916, **38**, 2533—2535).—A continuation of previous work (compare A., 1916, i, 710). The results obtained confirm the conclusions previously drawn, and show that the chloral- and butylchloral-alcoholates from primary alcohols are least highly dissociated, those of tertiary alcohols most highly dissociated, and those of secondary alcohols fall between them. W. G.

Manufacture of Acetals. A. T. KING and F. A. MASON (Brit. Pat., 101428; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—Acetals of the type $CH_3{\cdot}CH(OR)_2$, in which R is an alkyl radicle, are obtained by treating a mixture of acetaldehyde (20—50%) and an aliphatic alcohol with hydrated or dehydrated chlorides or nitrates of aluminium, beryllium, calcium, cerium, lithium, magnesium, manganese, thorium, etc. with or without addition of hydrochloric or other acid. Thus a saturated solution of sodium chloride (20 c.c.) and aluminium chloride (10 grams) are added to 50 c.c. of a mixture containing 40% aldehyde and 60% alcohol, together with 1 c.c. of concentrated hydrochloric acid, and the mixture shaken for some time; the upper layer is washed with water and then with sodium carbonate solution, dried successively over calcium chloride and potassium carbonate, and finally fractionated to obtain the acetal. H. W.

Montan Wax. AD. GRÜN and E. ULBRICH (*Chem. Zentr.*, 1916, **2**, 402—403; from *Chem. Umschau Fett Harz-Ind.*, 1916, **23**, 57—60).—The authors are led to the conclusion that the unsaponifiable portion of Montan wax consists of montanone.

An amyl-alcoholic solution of the wax was neutralised with amyl-alcoholic sodium hydroxide and reduced with sodium powder; analyses of the product (acid number, 19·04; saponification number, 83·5; hydroxyl number, 30·5; esterification number, 64·8) pointed to the conclusion that an alcohol had been formed which had become esterified by the montanic acid. Hydrolysis of a solution of the product in xylene by means of alcoholic potassium hydroxide yielded *montanol*, $CH(C_{27}H_{55})_2{\cdot}OH$, needles, m. p. 59—60°. The waxy, unsaponifiable portion of Montan wax, m. p. 59·6°, which does not contain an alcoholic hydroxyl group yielded montanol when reduced with sodium in amyl-alcoholic solution.

Montanic acid was converted into montanone according to the method of Easterfield and Taylor (T., 1911, **99**, 2302); the ketone

had m. p. 59·6° (Easterfield and Taylor give 97°), and was identical with the unsaponifiable portion of the wax.

Montanyl acetate forms needles, m. p. 56·5°. H. W.

Iron-Acetylacetone-Pyridine Compounds. R. F. WEINLAND and EDMUND BÄSSLER (*Zeitsch. anorg. Chem.*, 1916, **96**, 109—138).—Ferri-acetylacetone dissolves in water to a red solution, becoming violet with acids. These violet solutions do not yield definite compounds. In presence of pyridine, however, crystalline compounds may be obtained. The chlorides may be prepared (1) by dissolving anhydrous ferric chloride in absolute alcohol and adding acetylacetone and pyridine, (2) by dissolving ferric acetate in absolute alcohol, adding alcoholic hydrogen chloride, acetylacetone, and pyridine; (3) by warming precipitated and partly dried ferric hydroxide with alcoholic hydrogen chloride and adding the same compounds; (4) by heating ferri-acetylacetone with alcoholic hydrogen chloride and pyridine. All the products are violet with black reflex, and are decomposed by water, yielding red solutions and precipitating ferric hydroxide. They are soluble in many organic solvents, including pyridine, to red solutions.

In order to determine whether a complex anion is present, the compounds have been mixed in alcoholic solution with lithium nitrate, bromide, iodide, and perchlorate, and with sodium platinichloride, but without result. The chlorine may, however, be replaced by the thiocyanate radicle by mixing with lithium, magnesium, or ammonium thiocyanate in alcoholic solution. The complex thiocyanates crystallise with a green reflex, and are very sparingly soluble. The composition of the products does not allow of definite conclusions as to the constitution of the acetylacetone compounds. Most of the compounds may be represented as containing a complex cation with four atoms of iron.

In the formulæ below, (ac) represents the acetylacetone residue, $COMe{\cdot}CH{:}CMe{\cdot}O{-}$, Py represents pyridine, and in a single case (acac) represents the doubly enolised residue, $\underset{\substack{| \\ O \\ |}}{CMe}{:}CH{\cdot}\underset{\substack{| \\ O \\ |}}{C}{:}CH_2$.

The violet chloride, $\left[Fe_4\begin{matrix}Py_8\\(ac)_4\end{matrix}\right]Cl_8$, may be obtained by either of the methods described above, by mixing the reagents in suitable proportion. A reddish-violet chloride, containing acetylacetone attached by subsidiary valencies, has the composition

$$\left[\begin{matrix}Py_4\\Fe_4(ac)_4\\(acH)_4\end{matrix}\right]Cl_8,$$

and when dissolved in a mixture of chloroform and benzene deposits yellowish-green crystals of a pyridine salt of a tetrachloro- or pentachloro-ferric acid, $HFeCl_4$ or H_2FeCl_5.

Another reddish-violet chloride, $\left[\begin{matrix}Py_5\\Fe_4(ac)_4\\(acH)_3\end{matrix}\right]Cl_8$, is prepared from the chloride solution. Tetrachlorides may also be obtained,

$\left[Fe_4{}^{Py_4}_{(ac)_8}\right]Cl_4$ being reddish-violet and $\left[\begin{matrix}Py_3\\Fe_4(ac)_8\\(acH)\end{matrix}\right]Cl_4$ being red.

A red dichloride has the composition $\left[\begin{matrix}Py_3\\Fe_4(ac)_9\\(OH)\end{matrix}\right]Cl_2$.

The first-mentioned violet chloride yields with lithium thiocyanate, according to the proportions used, either $\left[Fe_4{}^{Py_8}_{(ac)_4}\right]^{Cl_4}_{(CNS)_4}$ or $\left[Fe_4{}^{Py_8}_{(ac)_4}\right](CNS)_8$. The reddish-violet octachloride or the red tetrachloride, in similar manner, yields $\left[Fe_4{}^{Py_4}_{(ac)_8}\right](CNS)_4$. By mixing ferric acetate and ammonium thiocyanate in acetylacetone and pyridine, the two compounds $\left[\begin{matrix}Py_8\\Fe_4(ac)_8\\O\end{matrix}\right](CNS)_2$ and

$$\left[Fe_4\begin{matrix}Py_4\\(acac)\\(CH_3{\cdot}CO_2)_5\\O\end{matrix}\right](CNS)_3$$

may be obtained. C. H. D.

Composition of Commercial Glucose and its Digestibility. J. A. Wesener and G. L. Teller (*J. Ind. Eng. Chem.*, 1916, **8**, 1009—1020).—Commercial glucose, or starch syrup, consists of a mixture of sugars and dextrins containing from 15 to 20% of water, about 0·06% of proteins, and a trace of mineral substances. The fermentable reducing sugars present are dextrose and maltose; two samples examined by the authors contained 11·7 and 17·2% of dextrose and 22·9 and 16·4% of maltose respectively. A third reducing substance, dextrin (or dextrins), is present, and this is not readily fermented by ordinary yeast, but may be made fermentable by the action of certain enzymes, especially those present in pancreatin, Takadiastase, and malt, as well as by the action of warm hydrochloric acid. The claim that glucose contains unfermentable reducing substances as reversion products, resulting from the action of acids on starch at high temperature, is untenable. Glucose consists, apparently, of substances which are wholly assimilable, and must be considered as a food having the nature of a sugar. W. P. S.

Preparation of Bromoacetylglucose and certain other Bromoacetyl Sugars. J. K. Dale (*J. Amer. Chem. Soc.*, 1916, **38**, 2187—2188).—A saturated solution of hydrogen bromide in acetic anhydride was found to react directly with several sugars, and from the reaction mixture the bromoacetyl derivative could be isolated. By this method bromoacetylxylose, bromoacetylcellulose, bromoacetyllactose, and bromoacetylglucose were obtained in crystalline form with yields of 26, 60, 60, and 77% respectively. Bromoacetylmaltose was only obtained in the amorphous condition by this method. W. G.

Nature of the Reducing Substances Precipitated by Basic Lead Acetate from Impure Sugar Solutions. H. PELLET (*Ann. Chim. anal.*, 1916, **21**, 217—223).—The precipitate produced when a molasses solution is treated with basic lead acetate contains a considerable quantity of a reducing substance. The latter consists of invert-sugar itself or a mixture of its constituent sugars; when the lead precipitate is separated and decomposed by sulphuric acid, the resulting solution is lævorotatory, the sugar it contains has the reducing power of invert-sugar, and is fermented completely by yeast. The reducing substance cannot be glutose, as stated recently by Davis (*J. Agric. Sci.*, 1916, **8**, 7), since this sugar is optically inactive and is not fermentable. If an invert-sugar solution is treated with equivalent quantities of basic lead acetate and sodium sulphate, the precipitate formed may contain up to 60% of the invert-sugar present, but the latter can be recovered by decomposing the precipitate with sulphuric acid. Normal lead acetate is recommended for the clarification of molasses solutions, calcium salts and excess of lead being removed from the solution before the copper-reducing power is estimated. W. P. S.

Volatile Organic Compounds, particularly Ethereal Oils, in the Manufacture of Sulphite Cellulose. ZOLTÁN KERTÉSZ (*Chem. Zeit.*, 1916, **40**, 945—948).—After reviewing the earlier investigations on the subject of the various volatile products formed in the commercial treatment of wood cellulose with alkali sulphite, the author describes the results of an examination of an ethereal, oily mixture, insoluble in water, obtained in this way from spruce. The oil, D_{15}^{15} 0·878, on distillation was found to consist mainly of cymene (approx. 80%), together with a sesquiterpene (10—12%), b. p. 136—138°/9 mm., $[\alpha]_D$ $-12·7°$, n_D 1·5124, D_{21}^{21} 0·9246, which gave a deep blue coloration with acetic anhydride and sulphuric acid (bromide, hydrogen haloids, and nitrosochlorides liquid), and a diterpene, D^{21} 0·950, n_D 1·5254, $[\alpha]_D$ $+4·9°$, b. p. 180—190°/9 mm.; the higher boiling fractions also contained a small quantity of an amorphous, colourless solid, m. p. 67°, possibly a polyterpene. It is believed that these hydrocarbons are produced by the reducing action of the sulphite on the resins of the wood accompanied by polymerisation, isomerisation, and dehydration under the conditions of the treatment.

In addition to fermentation products, therefore, the following volatile substances have been observed as by-products in the sulphite treatment of cellulose: acetaldehyde, acetone, methyl and ethyl alcohols, formic and acetic acids, furfuraldehyde, cymene, a sesquiterpene, and a diterpene. D. F. T.

Lignoceric Acid from Rotten Oak Wood. M. X. SULLIVAN (*J. Ind. Eng. Chem.*, 1916, **8**, 1027—1028).—Rotten oak bark, when subjected to dry distillation, yielded a distillate consisting of tarry matter mixed with a white, crystalline solid; the latter was separated by crystallisation from alcohol, and then washed with cold alcohol and with light petroleum. The crystals thus

obtained were treated with lithium acetate in methyl alcohol solution; the precipitate which formed was separated, decomposed with sulphuric acid, and the liberated acid crystallised from alcohol; it had m. p. 80—82°, and was identified as lignoceric acid. A small portion of the lithium salt was soluble in methyl alcohol; this was isolated, and yielded an acid, m. p. 85°, which appeared to be inactive cerebronic acid (compare Levene and Jacobs, A., 1912, i, 936). W. P. S.

Piperazine Cacodylate. ASTRUC (*Bull. Soc. chim.*, 1916, [iv], **19**, 392—395).—When piperazine (1 mol.) is evaporated in aqueous solution with cacodylic acid (2 mols.) to a syrupy consistency, *piperazine cacodylate*, $[AsOMe_2(OH)]_2,C_4H_{10}N_2,4H_2O$, is obtained as colourless crystals, m. p. 54—55°, which on further heating become dry and decompose at 100°, giving off water and piperazine. In aqueous solution, it gives a white precipitate with mercuric chloride, a brown precipitate with iodine in potassium iodide, and yellow precipitates with picric acid or uranium acetate. The salt is acid to phenolphthalein and alkaline to helianthin-A. W. G.

Amines. V. The Structure of Vitiatine. Synthesis of Methylethylenediamine. TREAT B. JOHNSON and GEORGE C. BAILEY (*J. Amer. Chem. Soc.*, 1916, **38**, 2135—2145).—If the constitution assigned to vitiatine,

$$\begin{matrix}NH\\NH_2\end{matrix}\!\!>\!C\cdot NMe\cdot CH_2\cdot CH_2\cdot NH\cdot C\!<\!\!\begin{matrix}NH\\NH_2\end{matrix},$$

by Kutscher (compare A., 1907, ii, 562, 708) is correct, this substance should, on hydrolysis, yield ammonia and methylethylenediamine. With the view of elucidating this point, the authors have succeeded in preparing this latter base by the following series of actions.

Benzylsulphonamide, when boiled with alcoholic potassium hydroxide for half an hour, gave a *potassium* salt, which when mixed with bromoethylphthalimide in the dry state and heated for five hours at 100—110° yielded *phthalimidobenzylsulphone-ethylenediamine*, $C_6H_4\!<\!\!\begin{matrix}CO\\CO\end{matrix}\!\!>\!N\cdot CH_2\cdot CH_2\cdot NH\cdot SO_2\cdot CH_2Ph$, slender prisms, m. p. 175—176·5°. This substance when alkylated with methyl iodide in methyl-alcoholic solution in the presence of sodium gave *phthalimidobenzenesulphonemethylethylenediamine*, slender prisms, m. p. 177—178°, which when hydrolysed with an excess of concentrated hydrochloric acid at 120° for four hours yielded *methylethylenediamine hydrochloride*, colourless, micaceous flakes, m. p. 130—132°, giving a *platinichloride*, tabular prisms, m. p. 240—242° (decomp.), and a *picrate*, prisms, m. p. 220—222° (decomp.). The free amine distils slowly with steam. In the course of the work, a number of other derivatives of benzylsulphonamide were prepared and examined.

The potassium salt of benzylsulphonamide when heated with ethylene dibromide for five hours at 130° gave *dibenzylsulphone-*

ethylenediamine, m. p. 202—204°, which with methyl iodide in the presence of alcoholic potassium hydroxide gave a mixture of *dibenzylsulphonedimethylethylenediamine*, m. p. 217—219°, and a very small amount of *dibenzylsulphonemethylethylenediamine*, m. p. 137°. The dimethyl derivative on hydrolysis with concentrated hydrochloric acid at 120—130° gave dimethylethylenediamine hydrochloride.

Bromoethylphthalimide when heated with the potassium salt of phenylsulphonamide for four hours at 100° gave *phthalimidophenylsulphone-ethylenediamine*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot CH_2\cdot NH\cdot SO_2Ph$, flat prisms, m. p. 175°.

By alkylation of benzylsulphonamide with the corresponding derivatives of benzyl chloride, the following compounds were prepared:

Benzylsulphondi-p-*nitrobenzylamide*, $CH_2Ph\cdot SO_2\cdot N(CH_2\cdot C_6H_4\cdot NO_2)_2$, needles, m. p. 193—194°, and *benzylsulphon*-p-*nitrobenzylamide*, m. p. 182—183°.

Benzylsulphondi-o-*nitrobenzylamide*, prisms, m. p. 169—170°, and *benzylsulphon*-o-*nitrobenzylamide*, m. p. 124—126°.

Di-*p*-nitrobenzylamine hydrochloride and the corresponding orthocompound were easily obtained by heating the corresponding sulphonamides with concentrated hydrochloric acid at 130—140°.

By the application of the method used by Johnson and Ambler for the synthesis of sarcosine (compare A., 1914, i, 264), the authors have prepared alanine. α-Bromopropionamide was digested in alcohol for six hours with the potassium salt of benzylsulphonamide, *benzylsulphonaminopropionamide*, $CH_2Ph\cdot SO_2\cdot NH\cdot CHMe\cdot CO\cdot NH_2$, prisms, m. p. 167°, was obtained, and on hydrolysis with a strong, boiling, aqueous solution of barium hydroxide yielded *benzylsulphonalanine*, $CH_2Ph\cdot SO_2\cdot NH\cdot CHMe\cdot CO_2H$, plates, m. p. 164—165°, which when heated with hydrochloric acid for two hours at 130° gave alanine hydrochloride. W. G.

The Pyrogenetic Decomposition of Amides. I. R. S. BOEHNER and C. E. ANDREWS (*J. Amer. Chem. Soc.*, 1916, **38**, 2503—2505).—Acid amides may be decomposed into the cyanides and water by heating them in a flask with substances such as aluminium oxide, pumice stone, or glass, the flask being provided with an outlet sufficiently high up to permit the volatile cyanide to distil off, while the amides condense and drop back on the hot contact material. Using aluminium oxide, the best proportions are 50 grams of oxide and 10 grams of amide, the temperature of the bath being about 250—260°, but varying with the amide. The time required is about four hours, and the yields obtainable vary from 54% in the case of benzamide to 72% in the case of hexoamide. Formamide under these conditions distilled off practically unchanged, and phenylacetamide sublimed over too readily. W. G.

The Pyrogenetic Decomposition of Amides. II. R. S. BOEHNER and A. L. WARD (*J. Amer. Chem. Soc.*, 1916, **38**, 2505—2507. Compare preceding abstract).—In this case the amides were passed in the form of vapour over the contact material heated in a tube, using a current of air to aid the passage of the amide. The most satisfactory temperature was found to be 425°, and the contact materials, placed in order of efficiency, were: pumice stone, sand, aluminium oxide, and graphite. In this case the decomposition was practically theoretical. W. G.

The Constitution of Carbamides. III. The Reaction of Urea and of Thiourea with Acetic Anhydride. Potassium Thiourea. EMIL ALPHONSE WERNER (T., 1916, **109**, 1120—1130. Compare T., 1915, **107**, 715; 1914, **105**, 924, etc.).—When urea is heated with acetic anhydride, the yield of acetylurea is poor, on account of the decomposition of the greater part of the urea with formation of acetamide and diacetamide, only that part of the urea which has undergone isomerisation to the form

$$NH{:}C(NH_2){\cdot}OH$$

becoming acetylated (compare T., 1913, **103**, 1014, 2281). The addition of sulphuric acid favours the production of this form from the cyclic form, $NH{\cdot}C{<}\begin{matrix}NH_3\\ |\\ O\end{matrix}$, which the author believes to represent the normal constitution of urea, and in the presence of a little sulphuric acid acetylurea can be obtained in a yield approaching 80% of the theoretical. Although urea cannot be converted into diacetylurea in one operation, acetylurea in the presence of sulphuric acid can be acetylated to diacetylurea of the probable constitution $NH{:}C(OAc){\cdot}NHAc$ (compare Kohmann, A., 1915, i, 944). Thiourea on treatment with acetic anhydride yields both the acetyl and the diacetyl derivative (compare Kohmann, *loc. cit.*), the formula given for the latter being analogous to that for the oxygen analogue, whilst the monoacetyl compound is regarded as an equilibrium mixture of the two forms, $\begin{matrix}C({:}NH)\\ |\\ S\end{matrix}{>}NH_2Ac$ and $NH{:}C(SH){\cdot}NHAc$. Potassium ethoxide and thiourea in the presence of alcohol react with formation of a *compound*, $CSN_2H_3K(CSN_2H_4)_2$, needles, m. p .145°. For experimental details see the original. D. F. T.

The Interaction of Aldehydes and Thiocarbamides in the Presence of Acids. AUGUSTUS EDWARD DIXON and JOHN TAYLOR (T., 1916, **109**, 1244—1262).—In acidic aqueous solution thiocarbamide reacts with acetaldehyde, giving a deposit of a *substance* of the composition $CSN_2H_2{:}CHMe$, due to the spontaneous decomposition of an intermediate unstable *iso*thiocarbamide base, $NH_2{\cdot}C({:}NH){\cdot}S{\cdot}CHMe{\cdot}OH$, the "*hydrochloride*" of which, $C_3H_8ON_2S,HCl$, is producible by the interaction of thiocarbamide and α-chloroethyl alcohol, and also of acetaldehyde and thiocarbamide hydrochloride. The insoluble reaction product from thiocarbamide and acetaldehyde may also be accompanied by a *sub-*

stance, $CSN_2H_2\colon CHMe,CHMe\colon O$. The series of changes giving rise to the main product is probably as follows: $CHMe\colon O + HCl \longrightarrow CHMeCl\cdot OH$;

$$CS(NH_2)_2 + CHMeCl\cdot OH \longrightarrow C(NH_2)_2\colon SCl\cdot CHMe\cdot OH \longrightarrow$$
$$HCl + NH_2\cdot C(\colon NH)\cdot S\cdot CHMe\cdot OH \longrightarrow H_2O + CSN_2H_2\colon CHMe.$$

The composition assumed for the intermediate unstable base is confirmed by that of the somewhat more stable *ethoxyethyl iminothiocarbamate*, $NH_2\cdot C(\colon NH)\cdot S\cdot CHMe\cdot OEt$, the *hydrochloride* of which is produced on treating an alcoholic solution of acetaldehyde containing thiocarbamide in suspension with hydrogen chloride.

The behaviour of formaldehyde towards thiocarbamide resembles that of acetaldehyde, the product being a colourless, subcrystalline *substance*, $CSN_2H_2\colon CH_2$, produced by dehydration of the intermediate base, which is even less stable than the corresponding acetaldehyde derivative. The action of hydrogen chloride on thiocarbamide in aqueous formaldehyde yields a syrupy *substance*, CSN_2H_4,CH_2O,HCl, which on neutralisation gave a *substance*, $CSN_2H_2\colon CH_2$, formed by the dehydration of the unstable base corresponding with the salt; the *picrate*, $C_2H_6ON_2S,C_6H_3O_7N_3$, analogous to the hydrochloride, is obtainable by the addition of formaldehyde to thiocarbamide in saturated picric acid solution.

Alkyl and aryl substituted thiocarbamides, when treated with hydrogen chloride in the presence of formaldehyde or acetaldehyde, likewise yield syrupy "*hydrochlorides*" of the same type as those derived from thiocarbamide itself; when their solutions are neutralised, the mono- and di-substitution derivatives give the corresponding bases and condensation products, whilst the tri- and tetra-substitution derivatives are unable to form condensation products. From acyl substituted thiocarbamides syrupy "*hydrochlorides*" are obtainable in a similar manner, but on account of the ease with which the bases undergo hydrolysis it was not found possible to prepare from them the corresponding condensation products; these, however, can be produced by the interaction of the acylthiocarbimides with aldehyde-ammonia in the presence of acetone, the *compounds* obtained from carbethoxythiocarbimide, carbomethoxythiocarbimide, and acetylthiocarbimide respectively according in composition with the formulæ $NH{<}{\begin{smallmatrix}CS\\CHMe\end{smallmatrix}}{>}N\cdot CO_2Et$,

$$NH{<}{\begin{smallmatrix}CS\\CHMe\end{smallmatrix}}{>}N\cdot CO_2Me \quad \text{and} \quad NH{<}{\begin{smallmatrix}CS\\CHMe\end{smallmatrix}}{>}NAc.$$

Methylene iodide and thiocarbamide in hot alcohol react readily with formation of an *iso*thiocarbamide *base*, $CH_2[S\cdot C(\colon NH)\cdot NH_2]_2$.

The constitution of the above "hydrochlorides," bases, and condensation products is discussed, together with the probable mechanism of the reactions observed in the formation and decomposition of the first-named.

Other compounds, such as benzaldehyde, salicylaldehyde, cinnamaldehyde, and certain ketones show evidence of condensation with thiocarbamide. For experimental details the original should be consulted.

D. F. T.

The Preparation of Nitriles. II. The Preparation of Aliphatic Nitriles. G. D. Van Epps and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1916, **38**, 2120—2128).—The method of preparing aromatic nitriles by heating the zinc salt of the acid with lead thiocyanates (compare A., 1910, i, 169) has been extended to the preparation of aliphatic nitriles. In addition, other metallic thiocyanates were used, and the results compared with those of lead thiocyanate. A wide range of metallic acetates was also tried in place of zinc acetate. Taking all the results into consideration, the best method is to use the zinc salt of the acid and lead thiocyanate in the proportion of one to two by weight. In the case of acetonitrile, the crude distillate is best purified by mixing it with half its volume of water, saturating it with solid potassium carbonate or ammonia gas, separating the top layer, and fractionating it. An excellent yield of acetonitrile is obtained by using cuprous thiocyanate in place of the lead salt. The yields are better with the acids of high molecular weight than with acetic acid, and a much larger yield is obtained from hydrocinnamic acid than from cinnamic acid. W. G.

The Preparation of Nitriles. III. The Catalytic Preparation of Nitriles. G. D. Van Epps and E. Emmet Reid (*J. Amer. Chem. Soc.*, 1916, **38**, 2128—2135).—Acetonitrile may be prepared by passing acetic acid vapour, mixed with a moderate excess of ammonia, over alumina or thoria at 500°, the yield reaching as much as 85%. The yield is variable, and depends on the activity of the catalyst and the velocity of the gases. The results show that 500° is the optimum temperature, and that alumina is a better catalyst than thoria. The presence of water in the acetic acid causes a diminution in the yield. When the acetic acid was replaced by acetone or ethyl acetate, no nitrile was obtained, and acetic anhydride gave lower yields than the acid itself. W. G.

Reactions under High Pressures. IV. Synthesis of Cyanides in the Electric Autoclave. Arthur Stähler (*Ber.*, 1916, **49**, 2292—2294).—In an earlier paper (A., 1913, ii, 697) the author described the production of boron nitrides by heating together boron trioxide and carbon in an atmosphere of nitrogen, in a special furnace capable of withstanding temperatures up to 2500° and pressures up to 500 atmospheres. The analogous production of cyanides has now been investigated.

Sodium and potassium carbonates when heated with carbon and nitrogen under 60 atm. pressure are converted to the extent of 95% into cyanides. Lithium cyanide may also be prepared in this way. The alkaline-earth carbonates mainly yield cyanamide under ordinary pressures, but only cyanides if the pressures are great. Magnesium, glucinum, and aluminium oxides give neither cyanides nor nitrides under these conditions. J. C. W.

Action of Sulphur on Naphthenes under Pressure. Walter Friedmann (*Chem. Zentr.*, 1916, ii, 485—486; from *Petroleum*, 1916, **11**, 978—982. Compare *Chem. Zentr.*, 1916, i, 1285).—Markovnikov and Spady have shown that when octa-

naphthene is heated with sulphur at 220—230° and the product subjected to nitration, trinitro-*m*-xylene is produced, and that during the first reaction small quantities of high-boiling products containing sulphur are also formed. The present investigation has been undertaken with the object of elucidating the mechanism of the transformation of naphthenes into aromatic hydrocarbons. *cyclo*Hexane has been heated under pressure with sulphur, and the product fractionated under diminished pressure. By nitration of the fractions of lowest boiling point, *m*-dinitrobenzene has been isolated; from the intermediate fraction, b. p. 40—60°/vacuum, thiophenol has been obtained, whilst the residue contains phenyl sulphide. Benzene cannot be identified among the products of the reaction, and it is probably not formed as an intermediate product. Without doubt the sulphur removes hydrogen, but the action only proceeds as far as dihydrobenzene, which is simultaneously oxidised and nitrated by the nitrating acid. The degradation of *cyclo*-hexane to *cyclo*hexadiene is represented by the scheme: $C_6H_{12} + S = C_6H_{11}{\cdot}SH$; $C_6H_{11}{\cdot}SH - H_2S \longrightarrow C_6H_{10}$ (*cyclo*hexene): $C_6H_{10} + S + H_2S \longrightarrow C_6H_{12}S_2$; $C_6H_{12}S_2 - 2H_2S \longrightarrow C_6H_8$ (*cyclo*hexadiene): $C_6H_8 + 2S + 2H_2S = C_6H_{12}S_4$; $C_6H_{12}S_4 - 3H_2S = C_6H_5{\cdot}SH$.

Methyl*cyclo*hexane has been similarly heated with sulphur and the product fractionated. The portions, b. p. 100·5—120°, yield trinitrotoluene, m. p. 82°, on nitration; thiocresol was isolated from the fraction, b. p. 80—130°/11 mm.

The different fractions obtained by distillation of the product of the interaction of sulphur and octanaphthene (1:3-dimethyl*cyclo*-hexane) react more or less strongly with bromine or permanganate. The portions, b. p. 30—90°/11 mm., yield trinitro-*m*-xylene, m. p. 181—182°, when nitrated; when the fraction, b. p. 90—100°/11 mm., is distilled at the ordinary pressure, thiol-*m*-xylenol, b. p. 210—215°, is obtained (the *mercury* salt, $[C_8H_9S_2]_2Hg$, crystallises in needles). The yield of thioxylenol is small; this is explained by the fact that it is accompanied by 3:3′-dimethyldibenzyl, which can be isolated by repeated fractionation of the portion, b. p. 110—180°/12 mm. This hydrocarbon is actually obtained when *m*-xylene is heated under pressure with sulphur, but it has not been proved if it can be obtained from a 1:3-dimethyl*cyclo*hexa-diene. It appears, therefore, probable that octanaphthene is in part converted into xylene as intermediate product when heated with sulphur. Genetic relationships between the aromatic and hydroaromatic hydrocarbons of petroleum are not known, and it is scarcely possible to account for the presence of both classes of sub-stance in oils. H. W.

Preparation of Benzene, Toluene, and other Aromatic Hydrocarbons from Petroleum and other Hydrocarbons. W. F. Rittmann (Brit. Pat., 1915, 9163; from *J. Soc. Chem. Ind.*, 1916, **35**, 1103).—Hydrocarbon oils are subjected to a temperature at which sudden gasification occurs and, whilst in the gaseous con-dition, are cracked at a temperature not less than 600°, preferably

650—800°, and at a pressure not less than 4·2 kilos. per sq. cm., preferably 17·6 kilos. per sq. cm. H. W.

Treatment of Xylene and other Aromatic Hydrocarbons to obtain Lower Hydrocarbons of the Same Series. SYNTHETIC HYDRO-CARBON Co. (Fr. Pat., 479786; from *J. Soc. Chem. Ind.*, 1916, **35**, 1103).—Xylene or other hydrocarbon is subjected, in form of a vapour, to a temperature not below 400° and a pressure not exceeding 14 kilos. per sq. cm. With higher temperatures (600—850°) a lower pressure, capable of being reduced to half an atmosphere, may be used. Under the latter conditions, 30% of toluene has been produced from xylene. H. W.

Preparation of Chloro-derivatives of Organic Substances. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Fr. Pat., 479645; from *J. Soc. Chem. Ind.*, 1916, **35**, 1131).—The substance to be chlorinated is heated with manganese dioxide and hydrochloric acid or with manganese dioxide, sulphuric acid, and a metallic chloride. For example, a mixture of benzene (200 kilos.), manganese dioxide (100 kilos.), and concentrated hydrochloric acid (400 kilos.) is heated at a temperature a little lower than the boiling point of benzene. H. W.

Halogenation. XIV. Bromination of Hydrocarbons by means of Bromine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1916, **38**, 2545—2552).—Bromination, like chlorination (compare A., 1915, i, 114), can be carried out by using a mixture of nitric and hydrobromic acids, but it is preferable to use a mixture of bromine and nitric acid. All the bromine enters the molecule, the nitric acid helping the oxidation of hydrogen bromide to bromine as soon as it is formed. Brominations are effected very rapidly and energetically. The method is specially suitable for moderately light hydrocarbons, the process not being so satisfactory with the higher ones, owing to the possibilities of nitration taking place.

With the calculated quantities of bromine and nitric acid acting for a short time, benzene yields bromobenzene, whereas if an excess of bromine and acid acts for a long time, the chief product is *p*-dibromobenzene. Toluene gives a mixture of *o*-bromotoluene and 3:4-dibromotoluene if the time allowed is short, and pentabromotoluene if an excess of bromine and nitric acid acts for a long time. *o*-Xylene yields respectively bromo-*o*-xylene and tetrabromo-*o*-xylene with *o*- and *p*-toluic acids; *m*-xylene yields respectively a mixture of bromo- and dibromo-*m*-xylenes and tetrabromoxylene, and *p*-xylene yields a mixture of bromo- and dibromo-*p*-xylenes, and tetrabromo-*p*-xylene with *p*-toluic acid, according as the time allowed for the action is short or long. Similarly, mesitylene yields respectively bromomesitylene and tribromomesitylene. On short bromination, ethylbenzene gives a mixture of *o*- and *p*-bromoethylbenzenes. W. G.

Mononitrohalogenobenzenes with Mobile Halogen. W. BORSCHE, L. STACKMANN, and J. MAKAROFF-SEMLJANSKI (*Ber.*, 1916, **49**, 2222—2243).—The reactivity towards sodioacetoacetic and

sodiomalonic esters of the halogen in the three pairs of compounds 4-bromo-3-nitrobenzonitrile and 5-bromo-2-nitro-*p*-toluonitrile, 4-bromo-3-nitroacetophenone and 2-chloro-5-nitro-4-methylacetophenone, and 4-bromo-3-nitro- and 2-bromo-5-nitro-benzophenones has been investigated. It is found, as usual, that the nitro-group confers greatest mobility on the halogen atom if it is adjacent to it, and that the activating influence of the cyano, acetyl, and benzoyl groups, whether ortho or para to the halogen, falls rapidly in the order given. The first and third compounds are easily obtained, and so other reactions have been studied with them.

One nitro-group is not sufficient to render a halogen atom active towards ethyl sodiomalonate, *o*-bromonitrobenzene, for example, being unaffected.

4-Bromo-3-nitrobenzonitrile is readily obtained by adding *p*-bromobenzonitrile to ice-cold fuming nitric acid. This reacts with an ethereal suspension of methyl sodiomalonate to form *methyl 2-nitro-4-cyanophenylmalonate*, $NO_2 \cdot C_6H_3(CN) \cdot CH(CO_2Me)_2$, in white leaflets, m. p. 129·5°, which is converted by boiling with a mixture of acetic acid and some 60% sulphuric acid into *2-nitro-4-carboxyphenylacetic acid*, $CO_2H \cdot C_6H_3(NO_2) \cdot CH_2 \cdot CO_2H$. This melts at 222° and changes into 2-nitro-*p*-toluic acid, and forms a *methyl* ester, in white leaflets, m. p. 76·5°. The above malonate, and also *methyl 2:4-dinitrophenylmalonate*, silvery leaflets, m. p. 95°, are stable towards ammonia.

Ethyl sodioacetoacetate reacts much more sluggishly than the malonate, but yields *ethyl 2-nitro-4-cyanophenylacetoacetate*, $NO_2 \cdot C_6H_3(CN) \cdot CHAc \cdot CO_2Et$, in stout, yellow needles, m. p. 85°. If gaseous ammonia is led into an ethereal solution of this, acetamide is deposited, and *ethyl 2-nitro-4-cyanophenylacetate*, pale yellow, glistening needles, m. p. 96°, is left in the solution. The ketone hydrolysis of the acetoacetate is achieved by boiling it with acetic acid and a little 60% sulphuric acid, whereby the cyano-group is also affected. *2-Nitro-4-carboxybenzyl methyl ketone* [*3-nitro-4-acetonylbenzoic acid*] forms long needles, m. p. 151·5°, and yields a *methyl* ester, in leaflets, m. p. 88·5°. The latter gives an orange-coloured *phenylhydrazone*, m. p. 116°, and reacts with benzenediazonium chloride in the presence of sodium acetate to form *a-phenylhydrazido-2-nitro-4-carbomethoxybenzyl methyl ketone*, $CO_2Me \cdot C_6H_3(NO_2) \cdot CAc{:}N \cdot NHPh$, in orange-coloured needles, decomp. 185°.

4-Bromo-3-nitrobenzonitrile reacts very readily with aniline in the presence of sodium acetate to form 2-nitro-4-cyanodiphenylamine. This may be reduced by means of tin and alcoholic hydrochloric acid to *2-amino-4-cyanodiphenylamine*,

$$NH_2 \cdot C_6H_3(CN) \cdot NHPh,$$

m. p. 154°, which reacts with acetic anhydride and sodium acetate to form *5-cyano-1-phenyl-2-methylbenziminazole*,

$$CN \cdot C_6H_3 <\genfrac{}{}{0pt}{}{N}{NPh}> CMe,$$

needles, m. p. 179°, and with nitrous acid to give *5-cyano-1-phenyl-*

aziminobenzene [9-*cyano*-1-*phenylbenzo*-1 : 2 : 3-*triazole*],

$$CN\cdot C_6H_3{<}{}^{N}_{NPh}{>}N,$$

colourless needles, m. p. 186°.

Piperidine reacts with the bromonitrobenzonitrile in the same way, giving 3-*nitro*-4-*piperidinobenzonitrile*, in brilliant, orange-coloured, stout needles, m. p. 110—111°, and this is readily hydrolysed by the above mixture of acetic and sulphuric acids to 3-*nitro*-4-*piperidinobenzoic acid*, yellow needles, m. p. 202—203° (decomp.). The nitrile is reduced by a cold solution of stannous chloride to 3-*amino*-4-*piperidinobenzonitrile*, m. p. 68—69°, b. p. 203—204°/16 mm., but tin and hydrochloric acid produce 6-*chloro*-3-*amino*-4-*piperidinobenzonitrile*, in white needles, m. p. 78—79°.

The bromonitrobenzonitrile also reacts with ammonia if heated with an alcoholic solution at 100°, and yields 3-*nitro*-4-*aminobenzonitrile*, in yellow needles, m. p. 159—160°. This may be hydrolysed as above to 3-nitro-4-aminobenzoic acid, or reduced to 4-*cyano*-o-*phenylenediamine*, m. p. 145—146°, which condenses with benzil to form 6-*cyano*-2 : 3-*diphenylquinoxaline*, $CN\cdot C_6H_3{<}{}^{N:CPh}_{N:CPh}$, m. p. 179—180°.

4-Bromo-3-nitrobenzonitrile differs from bromo-2 : 4-dinitrobenzene in its behaviour towards phenylhydrazine and potassium xanthate. With the former agent it gives a *compound*, $C_{26}H_{16}ON_8$, m. p. 168—169°, instead of the expected substance of the formula $CN\cdot C_6H_3{<}{}^{N}_{N}{>}NPh$, and with the latter it yields *di*-2-*nitro*-4-*cyanophenyl disulphide*, $(CN\cdot C_6H_3\cdot NO_2)_2S_2$, as a yellow powder, instead of a monosulphide.

5-Bromo-2-nitro-*p*-toluonitrile is conveniently obtained by nitrating the bromo-*p*-toluonitrile. The bromine atom in it is not very reactive, for methyl sodiomalonate gives only a very small yield of *methyl* 6-*nitro*-4-*cyano*-m-*tolylmalonate*,

$$NO_2\cdot C_6H_2Me(CN)\cdot CH(CO_2Me)_2,$$

as pale yellow, silky needles, m. p. 91°.

p-Bromoacetophenone is readily converted into 4-*bromo*-3-*nitroacetophenone*, m. p. 116·5°, by mixing a solution in concentrated sulphuric acid at −5° with fuming nitric acid. This reacts with methyl sodiomalonate to form *methyl* 2-*nitro*-4-*acetylphenylmalonate*, $NO_2\cdot C_6H_3Ac\cdot CH(CO_2Me)_2$, in stout, pale brown rhombohedra, m. p. 96°, and with aniline and anhydrous sodium acetate to give 2-*nitro*-4-*acetyldiphenylamine*, in orange-red, rhombic leaflets, m. p. 108—109°. This may be reduced by means of a boiling solution of stannous chloride in a mixture of acetic and hydrochloric acids to 2-*amino*-4-*acetyldiphenylamine*, pale yellow leaflets, m. p. 165—166°, which reacts with nitrous acid to form 5-*acetyl*-1-*phenylaziminobenzene* [5-*acetyl*-1-*phenyl*-1 : 2 : 3-*benzotriazole*], $C_6H_3Ac{<}{}^{N:N}_{NPh}$, m. p. 199—200°. This compound forms a sparingly soluble *oxime*, m. p. 222°, which is transformed by

phosphorus pentachloride into a *substance*, $C_{14}H_{11}ON_4Cl$, m. p. 265—267°.

4-Bromo-3-nitroacetophenone also reacts with piperidine to give 3-*nitro*-4-*piperidinoacetophenone*, in orange-red crystals, m. p. 90·5—91·5° (*oxime*, red needles, m. p. 122—123°), and with phenylhydrazine to yield merely the *phenylhydrazone*, $C_{14}H_{12}O_2N_3Br$, in red needles, m. p. 144—146°.

3-*Chloro*-p-*tolyl methyl ketone* is obtained from *m*-chlorotoluene and acetyl chloride as an oil, b. p. 127°/17 mm., which forms a *semicarbazone*, leaflets, decomp. 192—194°, and may be oxidised by alkaline permanganate to *o*-chloroterephthalic acid. When nitrated in sulphuric acid solution at −12° it yields 3:6-*chloronitro*-p-*tolyl methyl ketone*, in pale yellow needles, m. p. 75—76°, and this forms a *semicarbazone*, decomp. 215—217°, and a *phenylhydrazone*, slender, red needles, m. p. 127—129°. The nitrated ketone reacts with ethyl sodiomalonate to give *ethyl* 5-*nitro*-4-*acetyl*-m-*tolylmalonate*, $NO_2·C_6H_2MeAc·CH(CO_2Et)_2$, in pale yellow leaflets, m. p. 65—66°, with aniline to form *phenyl*-6-*nitro*-4-*acetyl*-m-*tolylamine*, $NO_2·C_6H_2MeAc·NHPh$, in slender, dark yellow needles, m. p. 135·5—136°, and with piperidine to yield 6-*nitro*-3-*piperidino*-p-*tolyl methyl ketone*, in long, orange-red prisms, m. p. 85°. The above nitrated diphenylamine may be reduced by tin and hydrochloric acid to *phenyl*-2-*amino*-4-*acetyl*-m-*tolylamine*, pale yellow leaflets, m. p. 112°, which forms an *acetyl* compound, $NHAc·C_6H_2MeAc·NHPh$, m. p. 78—80°.

4-Bromo-3-nitrobenzophenone, m. p. 124°, reacts very sluggishly with methyl sodiomalonate, and the isomeric 2-bromo-5-nitro-compound to no appreciable extent. The crude *methyl* 2-*nitro*-4-*benzoylphenylmalonate* is a dark brown, viscous oil, which may be hydrolysed by boiling with a mixture of acetic and sulphuric acids to form 2-*nitro*-4-*benzoylphenylacetic acid*, in white leaflets, m. p. 142°.

J. C. W.

Aromatic Nitro-derivatives. VI. General Considerations. M. Giua (*Gazzetta*, 1916, **46**, ii, 256—272. Compare A., 1916, i, 205).—The author discusses the results obtained in his five previous papers on the influence of nitro-groups in an aromatic nucleus on the replaceability of other groups present, reference being made to Laubenheimer's rule and to Koerner's rule. The various structures which have been suggested for the benzene ring are also discussed.

T. H. P.

Nitration of Toluene to Trinitrotoluene. Irwin W. Humphrey (*J. Ind. Eng. Chem.*, 1916, **8**, 998—999).—In the manufacture of trinitrotoluene it is generally preferred to make crude mononitrotoluene by nitrating toluene with a mixture of sulphuric acid (D 1·84) and nitric acid (D 1·42), and then to nitrate the mononitrotoluene to trinitrotoluene by treatment with more concentrated acids. In the latter part of the process, the best yields are obtained by operating at a temperature somewhat below 140°, using 98% sulphuric acid and concentrated nitric acid (D 1·52),

and maintaining the final nitrating mixture at 120—125° for two and a-half hours. The proportion of acids and toluene should be such that the water content of the final mixture is about 4·4%.

W. P. S.

Mixtures of Nitrated Explosives. II. M. GIUA (*Gazzetta*, 1916, **46**, ii, 272—277. Compare A., 1915, i, 950).—The system picric acid–2 : 4 : 6-trinitrotoluene does not form a compound; the eutectic, m. p. 55°, corresponds with 34% of picric acid. Further, camphor does not combine with 2 : 4 : 6-trinitrotoluene, but forms a simple eutectic, m. p. about 52°.

Uncertainty still prevails as regards the exact melting point of picric acid, and it would appear advantageous to employ in its place the solidifying point, for which more concordant results are obtainable.

T. H. P.

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. I. RALPH C. HUSTON and THEODORE E. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1916, **38**, 2527—2533).—When benzene is mixed with benzyl alcohol in equimolecular proportions and anhydrous aluminium chloride is added, a vigorous action occurs, the products being diphenylmethane, *p*-dibenzylbenzene, *o*-dibenzylbenzene, a hydrocarbon, $C_{27}H_{24}$, which is either tribenzylbenzene or methylenebisdiphenylmethane, $CH_2Ph \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot CH_2Ph$, and anthracene. By increasing the proportion of benzene used with respect to the benzyl alcohol, the yield of diphenylmethane is increased and of anthracene reduced. A rather large proportion of aluminium chloride is necessary.

With the view of confirming Verley's hypothesis as to the mechanism of the reaction between chloromethyl ethyl ether and benzene in the presence of aluminium chloride (compare A., 1899, i, 207), the authors have examined the action of aluminium chloride on mixtures of benzyl ethyl ether and benzene, chloromethyl ethyl ether and benzene, and on chloromethyl ethyl ether alone. In the first case, the products of the reaction were the same as with benzyl alcohol and benzene, but even at the end of a week 15% of unchanged benzyl ethyl ether was recovered. In the second case no benzyl ethyl ether was obtained. In the last case formaldehyde was obtained. They suggest as an alternative to Verley's hypothesis that the reaction is due to the preliminary formation of formaldehyde from the chloromethyl ethyl ether, and that this then reacts with the benzene to give diphenylmethane and anthracene.

W. G.

Amines. VI. The Utilisation of Hypochlorite Colour Reactions in Establishing the Mechanism of the Action of Methyl Sulphate on Aniline. NORMAN A. SHEPARD (*J. Amer. Chem. Soc.*, 1916, **38**, 2507—2514).—A careful examination of the action of methyl sulphate on aniline shows that the

course of the reaction is not that given by Werner (T., 1914, **105**, 2762), but that Ullmann's theory (compare A., 1903, i, 394) is correct. Using equimolecular proportions of the base and the sulphate as directed by Werner, the crystalline additive product was found to be the methyl hydrogen sulphate of the unalkylated base, $C_6H_5NH_2,MeHSO_4$, the yield being in accord with Ullmann's theory. Using Werner's quantities, the reaction at first proceeds according to the equation $2NH_2Ph + 2Me_2SO_4 = NH_2Ph,MeHSO_4 + NHMePh + Me_2SO_4$. The methylaniline is then converted into its methyl hydrogen sulphate,

$$2NHMePh + Me_2SO_4 = NHMePh,MeHSO_4 + NMe_2Ph,$$

and finally the dimethylaniline gives a methyl hydrogen sulphate.

The author has carefully examined the colour reactions of aniline and its methyl and dimethyl derivatives under differing conditions, and finds that the colours obtained vary considerably with the conditions. The characteristic test for aniline is the deep reddish-purple colour obtained by the addition of bleaching powder solution to a neutral aqueous solution of the base, and under these conditions methylaniline gives a yellow, murky solution, and dimethylaniline a colourless, murky solution. If the addition of the hypochlorite is followed by the addition of dilute sulphuric acid, methylaniline gives a very intense indigo-blue colour, and dimethylaniline a deep orange-yellow colour, both these colours being characteristic. If the acid is added first the same colour reactions occur, but the shade is not so intense in the case of methylaniline. In alkaline solution, methylaniline gives with bleaching powder solution a white precipitate with distinct navy-blue colour, developing slowly and then slowly fading to yellow, which is characteristic. W. G.

The Molecular Rearrangement of Triphenylmethylhalogenamines. ISABELLA VOSBURGH (*J. Amer. Chem. Soc.*, 1916, **38**, 2081—2095).—A number of triphenylmethylhalogenamines were prepared and their molecular rearrangements under various conditions studied with the view of obtaining fresh evidence in favour of Stieglitz's theory (compare this vol., i, 22) as to the method of these arrangements. *Triphenylmethylbromoamine*, $CPh_3 \cdot NHBr$, m. p. 63°, was prepared by brominating triphenylmethylamine in cold chloroform solution in the presence of 10% sodium hydroxide. It is reconverted by dry hydrogen chloride into triphenylmethylamine hydrochloride. When heated with soda-lime, calcium oxide, or sodium methoxide in methyl-alcoholic solution, the bromoamine is converted into phenyliminobenzophenone, $CPh_2{:}NPh$. Triphenylmethylamine was converted into its *benzoyl* derivative, m. p. 160—162°, in order to be able to test for the presence of this substance in the products of the previous rearrangement.

When triphenylmethylamine was added to a cold solution of hypochlorous acid and the mixture extracted with chloroform, *triphenylmethyldichloroamine*, $CPh_3 \cdot NCl_2$, m. p. 128°, was obtained, but all attempts to prepare the monochloroamine were unsuccessful.

This substance underwent molecular rearrangement when heated alone or with soda-lime, and in the latter case phenyliminobenzophenone was isolated from the products of the reaction.

Triphenylmethylmethylchloroamine, $CPh_3 \cdot NMeCl$, m. p. 102—104°, was prepared by the action of hypochlorous acid on triphenylmethylmethylamine hydrochloride in aqueous alcoholic solution. Attempts to cause it to undergo molecular rearrangement by the action of heat or alkalis were unsuccessful.

Diphenyl-p-*chlorophenylmethylamine* was prepared from the corresponding chloride, m. p. 86—89°, by passing dry ammonia gas into its hot benzene solution, and isolated in the form of its *hydrochloride*, m. p. 185—186°, giving a *platinichloride*, m. p. 155°. The hydrochloride was converted by the action of hypochlorous acid into *diphenyl*-p-*chlorophenylmethyldichloroamine*, $C_6H_4Cl \cdot CPh_2 \cdot NCl_2$, m. p. 110—112°, which by the action of heat alone or with soda-lime underwent molecular rearrangement, giving phenyliminochlorobenzophenone and chlorophenyliminobenzophenone in the molecular proportion of 3 : 1.

Attempts to cause a molecular rearrangement of benzophenonechloroimide, $CPh_2{:}N \cdot Cl$, which should by its constitution readily suffer this, according to Beckmann's theory, either by passing chlorine over the heated substance or by the action of phosphorus pentachloride, were unsuccessful. W. G.

The Molecular Rearrangement of some Triarylmethylchloroamines. AGNES FAY MORGAN (*J. Amer. Chem. Soc.*, 1916, **38**, 2095—2101).—An extension of Vosburgh's work (compare preceding abstract), a quantitative study being made of the molecular rearrangement of two substituted triphenylmethylchloroamines under the influence of soda-lime.

Phenyl-p-*dichlorophenylmethylamine hydrochloride*, m. p. 201°, was prepared by the action of dry ammonia gas on a hot benzene solution of phenyldi-*p*-chlorophenylmethyl chloride (compare Stagner, this vol., i, 23). By the action of hypochlorous acid this was converted into *phenyldi*-p-*chlorophenylmethylchloroamine*, $CPh(C_6H_4Cl)_2 \cdot NHCl$, m. p. 55°, which when heated with soda-lime gave a mixture of phenylimino-*pp'*-dichlorobenzophenone and *p*-chlorophenylimino-*p*-chlorobenzophenone in the molecular proportions of 1 : 2.

Phenyl-*p*-chlorophenyl-*p*-bromophenylmethyl chloride (compare Stagner, *loc. cit.*) was converted by the action of ammonia into *phenyl*-p-*chlorophenyl*-p-*bromophenylmethylamine*, isolated in the form of its *hydrochloride*, m. p. 196°, which by the action of hypochlorous acid was converted into *phenyl*-p-*chlorophenyl*-p-*bromophenylmethylchloroamine*, $C_6H_4Cl \cdot CPh(C_6H_4Br) \cdot NHCl$, not obtained in a solid form. This substance when heated with soda-lime gave a mixture of *p*-chlorophenylimino-*p*-bromobenzophenone, *p*-bromophenylimino-*p*-chlorobenzophenone, and phenylimino-*p*-chloro-*p'*-bromobenzophenone in equimolecular proportions.

W. G.

Rings containing a Triple Linking. III. Constitution of *cyclo*Succinyldiaminotolane. PAUL RUGGLI (*Annalen*, 1916, **412**, 1—13. Compare A., 1912, i, 914; 1913, i, 1106).—The object of the present investigation is to show that *cyclo*succinyldiaminotolane cannot be represented by the constitution

$$\begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{matrix} > N\cdot C_6H_4\cdot C\colon C\cdot C_6H_4\cdot NH_2 \text{ or}$$

$$\begin{matrix} CH_2\cdot CH_2 \\ | \\ CO \text{———} O \end{matrix} > C\colon N\cdot C_6H_4\cdot C\colon C\cdot C_6H_4\cdot NH_2,$$

either of which is possible in view of the method of preparation of the substance.

o′-*Nitro*-o-*aminotolane*, $NO_2\cdot C_6H_4\cdot C\colon C\cdot C_6H_4\cdot NH_2$, ruby-red needles, m. p. 118—119°, obtained together with *oo*′-diaminotolane and unchanged material by heating oo′-*dinitrotolane* with phenylhydrazine in xylene at 125—150°, is a weak base which forms a colourless *hydrochloride*, can be diazotised, and yields *oo*′-diaminotolane by further reduction. When treated with succinyl chloride under the conditions in which *oo*′-diaminotolane yields *cyclo*succinyldiaminotolane, it is converted, not into a substance having a constitution corresponding with either of those given above, but into *di*-o′-*nitrosuccinyldi*-o-*aminotolane*, $C_2H_4(CO\cdot NH\cdot C_6H_4\cdot C\colon C\cdot C_6H_4\cdot NO_2)_2$, tufts of yellow needles, m. p. 227—229° (decomp.).

o′-Nitro-*o*-aminotolane reacts with the hemi-chloride of ethyl succinate in boiling ether to form the *ester*,

$$NO_2\cdot C_6H_4\cdot C\colon C\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

yellow needles, m. p. 122·5—123·5°; attempts to convert this into a substance having a constitution corresponding with the former of those given above were unsuccessful, since by heating in a vacuum the substance remains practically unchanged at 240° and yields a pitch at higher temperatures. The failure to effect ring closure is probably to be attributed to the presence of a substituent in the ortho-position to the nitrogen atom. The o-*toluidide*, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Et$, prepared from *o*-toluidine and the hemi-chloride of ethyl succinate in ether, also does not lose ethyl alcohol at 300°, whereas the *anilide*,

$$NHPh\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

m. p. 56·5—57·5°, prepared in a similar manner, is converted into succinanil by heating at 220° for a few minutes.

The fact that succinyl chloride and aniline in cold dilute solution do not react to form succinanil is regarded as disproving the possibility that *cyclo*succinyldiaminotolane may have either of the two formulæ given above. C. S.

Molecular Rearrangements of β-Triphenylmethyl-β-methylhydroxylamines and the Theory of Molecular Rearrangement. JULIUS STIEGLITZ and BERT ALLEN STAGNER (*J. Amer. Chem. Soc.*, 1916, **38**, 2046—2068).—An exhaustive investigation has been made of the reaction examined by Stieglitz and Leech (A., 1914, i, 268), and it is now definitely shown that

methylaniline is formed in quantity by the hydrolysis of the product of the rearrangement of β-triphenylmethyl-β-methylhydroxylamine, and further that benzophenone is also obtained during this hydrolysis.

β-Diphenyl-p-bromophenylmethyl-β-methylhydroxylamine was prepared in the form of its hydrochloride by condensing diphenyl-*p*-bromophenylmethyl chloride with methylhydroxylamine hydrochloride. The free base, prepared by the addition of alkali to the hydrochloride, was heated on a water-bath in ethereal solution with phosphorus pentachloride for four hours, and from the product of rearrangement, on hydrolysis, methylaniline and bromomethylaniline hydrochlorides, benzophenone, and bromobenzophenone were isolated.

In the light of this and other recent work (compare Kuhara, A., 1914, i, 538; Jones, A., 1914, i, 253), the authors discuss very fully the various theories as to the mode of rearrangement in such reactions. They draw the conclusion that unless conclusive evidence is brought that salts, leading to the intermediate formation of salts of univalent nitrogen derivatives, are involved in their rearrangement, the rearrangement of triphenylmethylmethylhydroxylamine, the relation of stereoisomerism of oximes to their arrangement products, and the spontaneous rearrangement of the sulphonic ester of benzophenoneoxime (compare Kuhara, *loc. cit.*) would be inconsistent with the theory of the intermediate formation of univalent nitrogen derivatives in the rearrangement of hydroxylamines, and that the facts at present agree with Beckmann's theory of a direct exchange of radicles. Other facts, such as the rearrangement of azides, are, however, inconsistent with Beckmann's theory, but are in agreement with Stieglitz's theory (*loc. cit.*) of the intermediate formation of unsaturated nitrogen derivatives in the rearrangements of chloroamines, hydroxylamines, and azides. It is probable that both types of arrangements may take place. Common to both theories, and the most important feature in their present forms, is that the rearrangements originate from the tendency of unstable positive atoms, Cl^+, $-O^+$, $=N^+$, etc., to pass over into their stable negative forms, Cl^-, $-O^-$, $N^=$, by a capture of electrons from other atoms in the same molecule.

W. G.

The Molecular Rearrangement of Triarylmethylhydroxylamines. BERT ALLEN STAGNER (*J. Amer. Chem. Soc.*, 1916, **38**, 2069—2081).—A continuation of the study of the molecular rearrangement of halogenated triphenylmethylhydroxylamines under the influence of phosphorus pentachloride (compare preceding abstract). A quantitative examination of the products of hydrolysis of the phenyliminobenzophenones resulting from the rearrangement was made to determine the proportions of each aryl group migrating and the influence of substitution on this migration. Of the three hydroxylamines examined, diphenyl-*p*-bromophenylmethylhydroxylamine, like the corresponding chloro-compound, rearranged itself so that, roughly, in two-thirds of the rearranging

molecules a phenyl group, and in the remaining third a bromophenyl group, migrated. This ratio was reversed in the case of phenyl-dibromo- and -dichlorophenylmethylhydroxylamine. In the case of phenylchlorophenylbromophenylmethylhydroxylamine, roughly one-third of the rearranging molecules showed a migration of the chlorophenyl group, the bromophenyl group, and the phenyl group respectively. These results indicate that the halogens have no marked effect on the tendency of the aryl groups to migrate to the nitrogen.

Diphenyl-p-*bromophenylmethylhydroxylamine* was obtained by the interaction of diphenyl-*p*-bromophenylmethyl chloride in anhydrous benzene and hydroxylamine in concentrated alcoholic solution, and isolated in the form of its *hydrochloride*, m. p. 144—145° (decomp.). The free base is a pale yellow, viscous liquid.

Phenyldi-p-*chlorophenylmethylhydroxylamine hydrochloride*, m. p. 129—130° (decomp.), was similarly prepared. The free base is a pale yellow, syrupy liquid or gum.

Phenyldi-p-*bromophenylmethylhydroxylamine hydrochloride* has m. p. 75°. The free base is a yellow, viscous liquid.

The fourth hydroxylamine was prepared by the following process. *p*-Chlorobenzophenone dichloride was condensed with bromobenzene in the presence of aluminium chloride, the mixture being then poured on to ice. From the products, *phenyl*-p-*chlorophenyl*-p-*bromophenylcarbinol*, m. p. 91—93°, was isolated and converted into its *chloride*, m. p. 69—72°, by passing hydrogen chloride into a solution of the carbinol in carbon disulphide. This chloride was condensed with hydroxylamine as in the previous two cases, giving *phenyl*-p-*chlorophenyl*-p-*bromophenylmethylhydroxylamine hydrochloride*, softening at 45°, no sharp m. p. The free base was a yellow syrup. W. G.

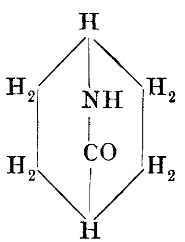
Aromatic Esters of Sulphurous Acid. M. M. Richter (*Ber.*, 1916, **49**, 2339—2345).—Aromatic esters of sulphurous acid are readily obtained by the action of thionyl chloride on the phenols in the presence of pyridine and in carbon disulphide solution. Diphenyl and ditolyl sulphites are stable, but the introduction of negative substituents lowers the stability. A new class of compounds is obtained if the sulphites are treated with sulphuric acid, and this reaction will be discussed in a future communication.

Phenyl sulphite, $SO(OPh)_2$, is a pale straw-yellow liquid, b. p. 185° (corr.)/15 mm. (slight decomposition; the crude substance is purer); o-*tolyl sulphite* has b. p. 192° (corr.)/13 mm., m-*tolyl sulphite*, b. p. 195—196° (corr.)/12 mm., and p-*tolyl sulphite*, b. p. 199° (corr.)/12 mm.; all are very stable towards water, alkali hydroxides, or ammonia. *Benzyl sulphite*, b. p. 193—199°/15 mm. (much decomposition), and *thymyl sulphite* are refractive oils. *α-Naphthyl sulphite*, m. p. 92—93°, is very stable towards alkalis, but is immediately hydrolysed by alcoholic ammonia, whilst *β-naphthyl sulphite*, a pearly powder, m. p. 79°, is very susceptible even to moisture. p-*Chlorophenyl sulphite*, b. p. 213—214°/12 mm., 2:4:6-*trichloro*-

phenyl sulphite, m. p. 87—88°, and 2 : 4 : 6-*tribromophenyl sulphite*, m. p. 130° (decomp.), are very susceptible to the influence of water and cannot be preserved. J. C. W.

The Silver Salt of Tri-iodophenol and its Catalytic Decompositions. G. H. WOOLLETT (*J. Amer. Chem. Soc.*, 1916, **38**, 2474—2478).—The author has prepared the silver salt of tri-iodophenol in a very pure state, but all the samples were yellow, and attempts to prepare Hantzsch's colourless form (compare A., 1908, i, 17) were unsuccessful. The salt when warmed with ethyl iodide decomposes in a manner exactly similar to that of the silver salt of tribromophenol (compare Hunter, A., 1916, i, 717), giving silver iodide and an unsaturated residue which polymerises to a white, amorphous oxide, $(C_6H_2OI_2)_n$. When treated with a very little iodine in water, the silver salt gives the red substance described by Lautemann (*Annalen*, 1861, **120**, 309). W. G.

Catalytic Hydrogenation of Hydroxy- and Amino-benzoic Acids. J. HOUBEN and ALEXANDER PFAU (*Ber.*, 1916, **49**, 2294—2299).—It is unnecessary to use glacial acetic acid as a solvent in the catalytic reduction of hydroxy- and amino-benzoic acids; in fact, it is very advisable not to do so, for these compounds suffer loss of water or ammonia to a considerable extent under such conditions. Even though the acid and its reduction product may be almost insoluble in water, they may be very easily reduced in suspension by hydrogen in the presence of platinum-black. Thus, *p*-aminobenzoic acid may be quantitatively reduced to *p*-amino*cyclo*hexane-carboxylic acid, which crystallises with $0{\cdot}5H_2O$ and sublimes at above 330°, but if quickly heated changes into the *lactam* (*isonortropinone*) (annexed formula), a very bitter substance, which forms very long needles, m. p. 191—192°.



Salicylic and anthranilic acids have also been reduced by this means, and accounts of many other applications of the process and of the products are promised. J. C. W.

Salts and Esters of the Nitrophenylacetonitriles. ST. OPOLSKI, Z. KOWALSKI, and J. PILEWSKI (*Ber.*, 1916, **49**, 2276—2283).—During recent years, the authors have isolated dark-coloured *potassium*, *sodium*, *silver*, and *methyl* salts of the three nitrophenylacetonitriles, similar to those obtained by Lifschitz and Jenner (A., 1916, i, 45). They regard them as being quinonoid in structure, especially in view of the fact that *o*- and *p*-nitrophenylacetic esters give similar salts (A., 1916, i, 815). The solutions are all violet, but become dark red or green in time.

o-Nitrophenylacetonitrile, m. p. 83·5—84°, is best obtained by Pschorr and Hoppe's method (A., 1910, i, 737), the necessary acetic acid being prepared by oxidising *o*-nitrophenylpyruvic acid, for which *o*-nitrotoluene is the starting point (Reissert, A., 1897,

i, 417). Attempts to prepare it from *o*-nitrobenzyl chloride or *bromide*, m. p. 42°, were fruitless. The para-compound, m. p. 115—116·5°, is obtained by nitration, and the meta-isomeride, m. p. 61—62°, from *m*-nitrobenzyl chloride.

In contrast with the violet methyl ester obtained from the freshly made silver salt (the *m*-ester is the most stable one), a colourless methyl compound can be formed by the action of methyl iodide on phenylacetonitrile in the presence of powdered sodium hydroxide, followed by nitration. This is *α*-p-*nitrophenylpropionitrile*, $NO_2{\cdot}C_6H_4{\cdot}CHMe{\cdot}CN$, m. p. 73—75°. J. C. W.

Semicarbazones of α-Ketonic Acids. αα-Di-iodo- and Dibromophenylbutyric Acids; α-Iodo- and α-Bromophenylcrotonic Acids. J. BOUGAULT (*Compt. rend.*, 1916, **163**, 481—483. Compare A., 1916, i, 817).—*αα-Di-iodo-γ-phenylbutyric acid*,

$$CH_2Ph{\cdot}CH_2{\cdot}CI_2{\cdot}CO_2H,$$

m. p. 145°, is readily obtained by the action of iodine on an alkaline solution of the semicarbazone of benzylpyruvic acid, and is isolated in the form of its *sodium* salt. An aqueous solution of its sodium salt, when heated at 100°, rapidly decomposes, giving the two *α-iodo-γ-phenylcrotonic acids*, $CH_2Ph{\cdot}CH{:}CI{\cdot}CO_2H$, of which the *stable* form has m. p. 105° and the *labile* form m. p. 100°. The labile acid is converted into the stable form by heating it at 100° for two hours with dilute hydrochloric acid.

αα-Dibromo-γ-phenylbutyric acid, m. p. 134°, is obtained as its *sodium* salt by the action of sodium hypobromite on a solution of the semicarbazone of benzylpyruvic acid. Like the di-iodo-compound, it is readily decomposed, giving two *α-bromo-γ-phenylcrotonic acids*, the *stable* form of which has m. p. 96° and the *labile* form m. p. 100°. The labile form is readily converted into the stable acid by the addition of a trace of bromine to its solution in carbon disulphide.

Both the *α*-iodo- and the *α*-bromo-phenylcrotonic acids readily yield γ-phenylcrotonic acid. W. G.

The Cinnamates of Tartaric Acid. The Question of Optically Active Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1916, **77**, 55—89).—It has been shown that when cinnamic acid is heated with tartaric acid at 168° an amorphous product soluble in sodium carbonate is obtained, which contains cinnamates. When cinnamoyl chloride or cinnamic anhydride is employed, products of similar physical properties are also obtained. If, however, *d*-tartaric acid is heated only at 105—110° with cinnamoyl chloride, the fused mass, after a certain interval, solidifies; a product is thereby obtained, which, instead of being lævorotatory, is dextrorotatory, and is, furthermore, insoluble in sodium carbonate. It can be recrystallised from light petroleum, and yields a product, m. p. 158—159°, with $[\alpha]_D + 282{\cdot}5°$ in acetone solution. This is the anhydride of the dicinnamate of tartaric acid, $C_{22}H_{16}O_7$. On heating alone above 110°, it is not converted into a lævorotatory product. If, however, the solidified

product from the original fusion, made at 105—110° is heated at 168°, an amorphous, lævorotatory product is obtained. Further investigation has shown that the dextrorotatory anhydride readily undergoes conversion when kept in solvents (chloroform or acetone) containing water into a lævorotatory, crystalline substance soluble in sodium carbonate, which can be recrystallised from benzene. This has m. p. 166—167°, and $[\alpha]_D$ $-275°$ in solution in sodium carbonate, and is the dicinnamate of tartaric acid, $C_{22}H_{18}O_8$. When the above reaction is carried out by heating together one molecule of tartaric acid with two molecules of cinnamoyl chloride, it is found that about one-third of the tartaric acid is recovered unchanged. A better yield is obtained when one molecule of tartaric acid is heated with three molecules of the chloride, and in this case cinnamic acid is obtained as a product of the reaction. This must therefore be represented by the following equation:

$$C_4H_6O_6 + 3C_9H_7OCl = 3HCl + C_9H_8O_2 + C_{22}H_{16}O_7.$$

When cinnamoyl chloride is heated under similar conditions with *l*-tartaric acid, an anhydride of a dicinnamate is also obtained. This is similar in its properties to the anhydride described above, but it is lævorotatory instead of dextrorotatory, the lævorotation and dextrorotation of the two substances being very nearly equal. The lævo-anhydride is also readily converted into a dicinnamate of tartaric acid, which is dextrorotatory, the dextrorotation being nearly equal to the lævorotation of the corresponding substance from *d*-tartaric acid.

The mechanism of the reaction between cinnamoyl chloride and the tartaric acids is discussed in some detail by the authors.

S. B. S.

Preparation of Carboxydisulphonic Acids from the Bisulphite Compounds of Unsaturated Aldehydes and Malonic Acid. OTTO NOTTBOHM (*Annalen*, 1916, **412**, 49—78).—In the reaction between malonic acid and the sodium hydrogen sulphite compound of glyoxal described by Behrend and ten Doornkaat Koolman (A., 1913, i, 8) the malonic acid cannot be replaced by methylmalonic, succinic, phenyl- or nitrophenyl-acetic acid, and the aldehyde must be such that its bisulphite compound is not, or at least not easily, hydrolysed under the experimental conditions. Such aldehydes are unsaturated ones which combine with two molecules of alkali hydrogen sulphite, and the behaviour of these additive compounds with malonic acid and with potassium hydrogen malonate has been examined.

When potassium α-hydroxy-γ-phenylpropane-αγ-disulphonate, prepared by heating at 130° the residue obtained by evaporating the solution of cinnamaldehyde (1 mol.) in boiling concentrated potassium hydrogen sulphite (2 mols.), is boiled with an equal molecular quantity of malonic acid and water for some time, sulphur dioxide is evolved and a by-product crystallises, even while the solution is boiling, the two main products, however, remaining in the cold mother liquor. The by-product proves to be *potassium*

hydrogen δ-sulpho-δ-phenyl-Δ^{α}-pentenoate,

$SO_3K\cdot CHPh\cdot CH_2\cdot CH{:}CH\cdot CO_2H$,

anhydrous needles; the *calcium* and the *barium* salts are described, and from the latter the free *acid* is obtained as a viscous syrup. When the acid or the potassium salt in aqueous solution is treated with bromine, addition, followed by elimination of hydrogen bromide, appears to occur, and *α-bromo-δ-sulpho-δ-phenyl-Δ^{α}-pentenoic acid*, $SO_3H\cdot CHPh\cdot CH_2\cdot CH{:}CBr\cdot CO_2H$, colourless needles, decomp. 203—205°, is obtained, which dissolves only slowly in aqueous sodium carbonate and forms a *methyl* ester, m. p. 165—166°, and *ethyl* ester, $C_{13}H_{15}O_5BrS$, m. p. 162—163·5°, both glistening leaflets insoluble in aqueous sodium carbonate.

The main products of the preceding reaction (which are the only products when potassium hydrogen malonate is used instead of malonic acid) remain in the mother liquor. By evaporating the solution to dryness, heating the residue at 150° for some hours (whereby carbon dioxide is evolved), and crystallising the product from glacial acetic acid, two substances are obtained. The one which is the less soluble is *dipotassium hydrogen βδ-disulpho-δ-phenylvalerate*, $SO_3K\cdot CHPh\cdot CH_2\cdot CH(SO_3K)\cdot CH_2\cdot CO_2H$, needles, whilst the more soluble is an isomeric *salt* which could not be obtained crystalline. The respective *acids*, obtained by means of concentrated hydrochloric acid, are viscous syrups, from which the only crystalline derivatives obtainable are the *aniline* salts of the *anilidodisulphonic acids*,

$NH_2Ph,SO_3H\cdot CHPh\cdot CH_2\cdot CH(SO_3H,NH_2Ph)\cdot CH_2\cdot CO\cdot NHPh$,

m. p. 240—242° (decomp.), quadratic leaflets, and 278—281° (decomp.), slender needles, respectively, prepared by boiling the acids with aniline. By fusion with potassium hydroxide and a little water on the water-bath the anilides both yield the same *substance*, C_9H_8O, colourless needles, m. p. 188°, the constitution of which has not yet been determined. If hydrolysed with boiling 20% hydrochloric acid before being fused with potassium hydroxide the two anilides, as do also the two acids under the same conditions, yield cinnamenylacrylic (δ-phenyl-$\Delta^{\alpha\gamma}$-pentadienoic) acid. The two sulpho-groups in the two acids are assumed to be in the β- and δ-positions, and the two acids are assumed to be stereoisomeric.

By treatment similar to that described above, potassium α-hydroxypropane-αγ-disulphonate (from acraldehyde and potassium hydrogen sulphite) and potassium hydrogen malonate or malonic acid also yield two salts, one of which is *dipotassium hydrogen βδ-disulphovalerate*, $SO_3K\cdot CH_2\cdot CH_2\cdot CH(SO_3K)\cdot CH_2\cdot CO_2H$, crystals, whilst the other isomeric salt has only been obtained as a syrup. The acids prepared from these two salts are syrups, and only that prepared from the crystalline salt yields the *aniline* salt of the *anilido-acid*,

$NH_2Ph,SO_3H\cdot CH_2\cdot CH_2\cdot CH(SO_3H,NH_2Ph)\cdot CH_2\cdot CO\cdot NHPh$,

crystals, m. p. 239—242° (decomp.). Both acids yield vinylacrylic ($\Delta^{\alpha\gamma}$-pentadienoic) acid by fusion with potassium hydroxide on the water-bath.

The reaction between dipotassium α-hydroxybutane-$\alpha\gamma$-disulphonate (from crotonaldehyde and potassium hydrogen sulphite) and malonic acid or potassium hydrogen malonate appears to yield only one acid, *$\beta\delta$-disulphohexoic acid*,

$$SO_3H\cdot CHMe\cdot CH_2\cdot CH(SO_3H)\cdot CH_2\cdot CO_2H,$$

a brown syrup, of which the only crystalline derivative obtained is the *aniline* salt of the *anilido-acid*,

$$NH_2Ph,SO_3H\cdot CHMe\cdot CH_2\cdot CH(SO_3H,NH_2Ph)\cdot CH_2\cdot CO\cdot NHPh,$$

rectangular leaflets, m. p. 245—248° (decomp.). The latter yields a *substance*, C_6H_6O, quadratic leaflets, m. p. 155—156°, by fusion with potassium hydroxide and a little water on the water-bath, but when hydrolysed with hydrochloric acid previously to the fusion yields sorbic acid in about 50% yield; the crude potassium disulphohexoate also yields sorbic acid to about the same extent by fusion with potassium hydroxide as above. C. S.

Desmotropic Forms of Bromocyanophenylpyruvic Esters. ST. OPOLSKI, L. CZAPOROWSKI, and J. ZACHARSKI (*Ber.*, 1916, **49**, 2283—2292).—The influence of a carbonyl group in the side-chain on the ability of phenylacetonitrile to exist in tautomeric forms has been examined. Both ethyl *o*-bromocyanophenylpyruvate and the *p*-bromo-compound can be isolated in a colourless ketonic form and a coloured enolic modification, thus:

$$C_6H_4Br\cdot CH(CN)\cdot CO\cdot CO_2R$$

and $C_6H_4Br\cdot C(CN):C(OH)\cdot CO_2R$.

Ethyl oxalate and *p*-bromophenylacetonitrile are warmed with a solution of sodium ethoxide, and the sodium salt of the *ethyl* p-*bromocyanophenylpyruvate* separates on cooling. The *keto*-ester is obtained in colourless crystals, m. p. 147·5°, if a solution of this salt is acidified with acetic acid, but the *enolic* ester is deposited if a solution in an excess of alkali hydroxide is mixed with dilute hydrochloric acid at 0°, as an orange-coloured precipitate, m. p. 60° (decomp.). The enol dissolves quickly in sodium carbonate solution, and reacts with bromine and ferric chloride, but the ketone dissolves slowly and does not give the other reactions. The *sodium*, *potassium*, *ammonium*, and *silver* salts are yellow; phenylhydrazine gives bromine-free compounds, m. p. 260° and m. p. 119—120°, under some conditions, but the true *phenylhydrazone* is formed in yellow crystals, m. p. 118°, if a concentrated solution of the ester in acetic acid is warmed with one equivalent of the base.

o-Bromophenylacetonitrile, m. p. 0—1°, b. p. 145—147°/14 mm., reacts in the same manner to form *ethyl* o-*bromocyanophenylpyruvate*; the colourless *keto*-ester has m. p. 140—142°, the yellow *enolic* ester has m. p. 98—120° (decomp.), whilst the *sodium* and *silver* salts are pale yellow. The phenylhydrazone could not be isolated, the products being the above compounds, m. p. 260° and m. p. 119—120°, which are recognised as the diphenylhydrazide of oxalic acid and the phenylhydrazide of ethyl hydrogen oxalate.

In the preparation of the enolic ester the precipitate is quickly removed by filtration. It is then observed that colourless crystals,

m. p. 82°, are deposited by the mother liquor, which change after contact with the solution for a longer time into others with m. p. 148—150°. These two substances are free from nitrogen, and are probably desmotropic forms of *o*-bromophenyloxalacetic acid, $C_6H_4Br\cdot CH(CO_2H)\cdot CO\cdot CO_2H$. J. C. W.

Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acid and Trichlorodiethylaminoxanthonecarboxylic Acid and some of their Derivatives. W. R. ORNDORFF and C. C. ROSE (*J. Amer. Chem. Soc.*, 1916, **38**, 2101—2119. Compare Basler Chemische Fabrik., 1896, D.R.-P., 85931, 87068; Haller and Umbgrove, A., 1901, i, 644).—An investigation as to the best method of preparing diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and of its properties.

When diethyl-*m*-aminophenol is condensed with tetrachlorophthalic anhydride under such conditions that tetrachlororhodamine is not formed, either by heating the two substances in toluene according to the German method (*loc. cit.*) or by heating them together without a solvent (compare Haller and Umbgrove, *loc. cit.*), the product is made up of two molecules of the aminophenol and one of the anhydride, and not of one molecule of each substance as stated by the latter authors. The product is *hydroxyphenyldiethylammonium diethylamino-*m*-hydroxybenzoyltetrachlorobenzoate*,

$$OH\cdot C_6H_3(NEt_2)\cdot CO\cdot C_6Cl_4\cdot CO_2\cdot NHEt_2\cdot C_6H_4\cdot OH,$$

prisms having a faint yellow tinge, m. p. 198° (decomp.). It dissolves in alkali or ammonium hydroxides with a yellow colour, which gradually darkens, and after a time the trichloro-acid (see below) is deposited as a bright yellow precipitate. The benzoate, if dissolved in cold 5% aqueous sodium hydroxide and the solution immediately poured into dilute sulphuric acid, or dissolved in cold concentrated sulphuric acid and the solution poured into ice water, is decomposed, giving diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid, light yellow prisms, m. p. 217°, already described by the previous workers (*loc. cit.*). When dry ammonia is passed over this acid it absorbs two molecules of the ammonia, losing one again when dry air is passed over it, giving an *ammonium* salt. It forms a yellow *silver* salt, a pale yellow *methyl* ester, m. p. 146—148°, and an *ethyl* ester, m. p. 120°. When heated with acetic anhydride on a water-bath for seven hours the acid gives a mixture of a true *diacetate*, $CO{<}{\scriptsize\begin{matrix}-O-\\C_6Cl_4\end{matrix}}{>}C{<}{\scriptsize\begin{matrix}OAc\\C_6H_3(NEt_2)\cdot OAc\end{matrix}}$, m. p. 230—231°, which is colourless, and a *monoacetate*,

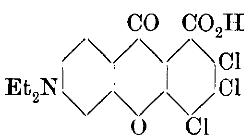
$$OAc\cdot C_6H_3(NEt_2)\cdot CO\cdot C_6Cl_4\cdot CO\cdot OAc,$$

of the mixed anhydride of the tetrachloro-acid and acetic acid, which is yellow and has m. p. 174—180°, the true diacetate being a derivative of the tautomeric form of the acid; the absence of colour is due to the fact that the ketonic group is no longer present. The monoacetate when boiled for six hours with ethyl alcohol gave the *ethyl* ester of the true monoacetate, m. p. 190—192°, and with

methyl alcohol the *methyl* ester, m. p. 152—155°, both of which were yellow.

Dry hydrogen chloride, when passed over the dry tetrachloro-acid, is absorbed to the extent of slightly more than one molecule, giving a colourless substance, which when exposed to dry air loses its excess of acid and leaves a yellow *hydrochloride*. The excess of hydrogen chloride is loosely attached to the ketonic group, giving an oxonium or a carbonium salt. The methyl ester of the tetra-chloro-acid takes up two molecules of hydrogen chloride under similar conditions, giving a colourless *dihydrochloride*, which when exposed to dry air loses one molecule of hydrogen chloride and gives a yellow *hydrochloride*. The methyl ester of the monoacetate of the tetrachloro-acid similarly gives a colourless *dihydrochloride*, which changes to a yellow *hydrochloride* with loss of hydrogen chloride.

When the tetrachloro-acid is dissolved in 3% aqueous potassium hydroxide and the solution is brought to the boil, the *potassium* salt of 2 : 3 : 4-*trichloro*-6-*diethylaminoxanthone*-1-*carboxylic acid* (annexed formula) is precipitated. It crystallises from methyl or ethyl alcohol in yellow needles, m. p. 285°, containing $2H_2O$. The free *acid* is obtained by decomposing the potassium salt with hydrochloric acid in boiling aqueous solution. From methyl alcohol it is obtained with 1MeOH, yellow needles, m. p. 278°, and from ethyl alcohol with no solvent of crystallisation. From a suspension of the potassium salt in cold water the acid is precipitated as a *hydrate*,



$$C_{17}H_{13}O_2NCl_3\cdot CO_2H,H_2O.$$

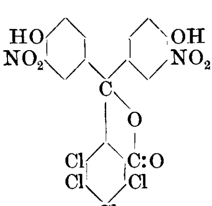
With dry ammonia the acid gives an *ammonium* salt, which is hygroscopic. When boiled with acetic anhydride, the free acid gives a mixed *anhydride*, $C_{17}H_{13}O_2NCl_3\cdot CO\cdot OAc$, yellow needles, m. p. 188—190°, which is converted by boiling acetone into an *acetonate*, a yellow powder, m. p. 185°. The mixed anhydride, when dried at 120°, gives a *hydrochloride*, which is pale yellow. When boiled with ethyl alcohol, the anhydride is converted into the free acid. Attempts to prepare a methyl ester of the trichloro-acid by the catalytic method of esterification were not successful. The dry trichloro-acid does not absorb hydrogen chloride, but concentrated hydrochloric acid turns it white without dissolving it.

W. G.

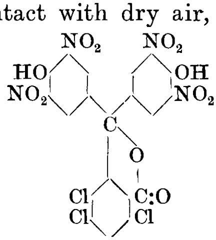
The Nitration Products of Phenoltetrachlorophthalein and some of their Derivatives. W. R. ORNDORFF and J. J. KENNEDY (*J. Amer. Chem. Soc.*, 1916, **38**, 2486—2503).—The authors have investigated the nitration products of phenoltetra-chlorophthalein and their derivatives to study the effect of introducing negative groups into the phthalein molecule. The same yield of phenoltetrachlorophthalein (compare Orndorff and Black, A., 1909, i, 389) was obtained by using tetrachlorophthalic acid in place of the anhydride, and the same amount of tetrachlorofluoran

was also formed. When boiled with benzoyl chloride, phenoltetrachlorophthalein gives a *dibenzoate*, m. p. 213°, which crystallises from benzene as a *hydrate* containing $1H_2O$. This same dibenzoate, but no monobenzoate, is obtained by the Schotten-Baumann reaction. When phenoltetrachlorophthalein is heated with a mixture of glacial acetic acid (10 parts) and sulphuric acid (1 part) for one hour at 80°, the mixture cooled to 20°, and nitric acid (D 1·42) gradually added, keeping the temperature below 50°, *dinitrophenoltetrachlorophthalein*, light yellow crystals, m. p. 240°, is obtained, which is soluble in alkali hydroxides and carbonates, but insoluble in alkali hydrogen carbonates. The dinitro-compound when exposed to dry ammonia absorbs four molecules of ammonia, which it readily loses when exposed to air. It gives a *dibenzoate*, m. p. 205°, forming a *hydrate* containing $1H_2O$, and a *diacetate*, m. p. 136°, crystallising from benzene with $2H_2O$ and from acetone with $1H_2O$. When brominated in acetic acid solution, the liquid being heated until the dinitro-compound just dissolves, *bromodinitrophenoltetrachlorophthalein*, m. p. 220—221°, is obtained. It absorbs five molecules of ammonia, losing three when a current of dry air is passed over it. The diammonium salt is not stable and gradually loses ammonia when kept. *Dibromodinitrophenoltetrachlorophthalein* was obtained by using slightly more bromine and boiling the solution for two hours after all the dinitro-compound had dissolved. It has m. p. 271—272° and is less soluble in the usual solvents than the monobromo-derivative. It absorbs five molecules of ammonia, losing three readily and the last two slowly when kept. When dinitrophenoltetrachlorophthalein is reduced in alcoholic solution by stannous chloride and hydrochloric acid, it yields *diaminophenoltetrachlorophthalein* as a coffee-brown, crystalline powder, m. p. above 335°, which dissolves in alkalis, giving a Prussian-blue colour, which disappears on keeping. The base gives a colourless *dihydrochloride*, which is dissociated by boiling its aqueous solution.

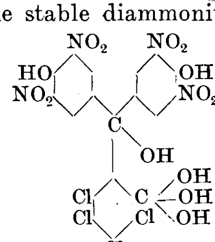
When phenoltetrachlorophthalein is heated for one hour at 80—90° with sulphuric acid (D 1·84), the solution cooled to 0°, and a mixture of equal weights of nitric acid (D 1·42) and sulphuric acid added, the temperature being allowed to rise to 35°, the product is *tetranitrophenoltetrachlorophthalein*, pale yellow needles, m. p. 289—290°. It crystallises from acetone with $2H_2O$. In contact with dry ammonia it absorbs five molecules of the gas, losing only three in contact with dry air, the stable diammonium



(I.)

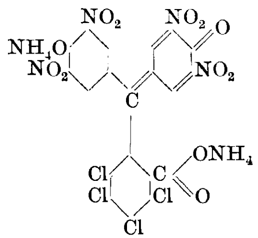


(II.)



(III.)

salt being deep orange in colour. It gives a *dibenzoate*, m. p. 285°, and a *diacetate*, m. p. 200°, and on reduction yields *tetra-aminophenoltetrachlorophthalein*, a light brown, crystalline powder, m. p. above 335°. It is more soluble in ordinary solvents than the diamino-compound, but its solutions in alkalis are not such an intense blue. Tetranitrophenoltetrachlorophthalein, unlike the dinitro-compound, is soluble in alkali hydrogen carbonates, as well as in the alkali hydroxides and carbonates. The authors assign the following constitutions to the dinitro- (formula I) and tetra-nitro-derivatives (formula II), and consider that the dihydrate of the tetra-nitro-compound can be best represented as a hydrate of the carbinol carboxylic acid (formula III). The stable di-ammonium salt of the tetranitro-compound is best represented by the quinonoid formula (IV).



(IV.)

Of the nitro-compounds prepared, the tetranitro-compound has the strongest acid properties, the dinitro-compound the weakest, and the bromo-dinitro- and dibromodinitro-compounds are intermediate between these two.

W. G.

Phthalonic Acid and its Derivatives. JOSEPH TCHERNIAC (T., 1916, **109**, 1236—1243).—A description of certain reactions of phthalonic acid (Tcherniac, D.R.-P., 79693, 86914; Graebe and Trümpy, A., 1898, i, 318). Phthalonic acid behaves as a mono-basic acid towards methyl-orange and as a dibasic acid towards phenolphthalein; it is readily oxidisable to phthalic acid, and when heated with acetic anhydride yields phthalonic anhydride, which reacts with a cold aqueous solution of ammonia, forming a *substance*, $C_9H_7O_4N$. A mixture of phthalonic acid, potassium hydroxide, and potassium cyanide in aqueous solution, when gradually saturated with carbon dioxide, gives the colourless *amide*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{O}>CH\cdot CO\cdot NH_2$, of phthalidecarboxylic acid. With sodium hydrogen sulphite in aqueous solution at 80°, sodium phthalonate yields a *sodium* salt, $C_8H_7O_6SNa,H_2O$, which is converted by aqueous ammonia into a substance, $C_8H_7O_2N$, probably identical with aminophthalide. The constitution of the sodium salt is probably $C_6H_4<\genfrac{}{}{0pt}{}{CH(SO_3Na)}{CO}>O,2H_2O$; in its formation a small quantity of a yellow *substance*, m. p. 232°, was obtained.

Details are given of a convenient bath to work at any constant temperature up to 400°, the contents of the bath consisting of potassium thiocyanate and water.

For experimental details the original should be consulted.

D. F. T.

The Hydroaromatic Ketones obtained from Phenols and Chloroform, and their Transformations. K. VON AUWERS (*Ber.*, 1916, **49**, 2389—2410. Compare A., 1907, i, 399; 1908, i, 550, etc.). It has already been shown that when 1-methyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-one is treated with magnesium methyl or ethyl haloids, it is converted into carbinols of the formula I, which change on heating into benzenoid compounds of the formula II.

$$CHCl_2\cdot CMe<\begin{matrix}CH:CH\\CH:CH\end{matrix}>C(OH)\cdot CH_2R \longrightarrow C_6H_4Me\cdot CHR\cdot CHCl_2.$$
(I.) (II.)

The reaction with other Grignard agents has now been investigated in order to see whether carbinols are always formed or whether, as in the case of the *o*-ketones, the radicle is introduced into the meta-position, thus:

$$CH\leqslant\begin{matrix}CH{=}CH\\CH{-}CO\end{matrix}>CMe\cdot CHCl_2 \text{ gives}$$
$$R\cdot CH_2\cdot CH<\begin{matrix}CH{=}CH\\CH_2{-}CO\end{matrix}>CMe\cdot CHCl_2.$$

It is found that the propyl, *iso*propyl, and benzyl compounds give carbinols in the normal way, but that in the case of the *iso*propyl derivative a small amount of an unsaturated ketone is also formed, according to the alternative scheme. Even the carbinol obtained in this case has peculiar properties, for the dichloroalkylbenzene which it yields on heating is a mixture of the expected one with another, in which the dichloromethyl group seems to be united directly to the ring.

1-Methyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-one, from *p*-cresol, forms an *oxime*, in leaflets, m. p. 65—66°. When treated with double the theoretical quantity of magnesium propyl bromide or iodide, it is transformed into 1-*methyl*-1-*dichloromethyl*-4-n-*propyl*-$\Delta^{2:5}$-cyclo*hexadien*-4-*ol*, $CHCl_2\cdot CMe<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CPr\cdot OH$, which crystallises in white prisms, m. p. 79°, and changes on heating at 145° into *aa-dichloro-β*-p-*tolylbutane*, b. p. 134°/15 mm., $D_4^{19\cdot8}$ 1·1117, n_α 1·52404, n_D 1·52827, n_β 1·53900, n_γ 1·54787 (all at 19·8°), and on boiling with alcoholic potassium hydroxide into *β-chloro-4-methyl-a-ethylstyrene*, $C_6H_4Me\cdot CEt:CHCl$, b. p. 117—118°/15 mm., $D_4^{19\cdot85}$ 1·0362, n_α 1·53639, n_D 1·54177, n_β 1·55548, n_γ 1·56777 (at 19·85°). The styrene yields *p*-tolyl ethyl ketone on oxidation; b. p. 113°/14 mm., $D_4^{21\cdot7°}$ 0·9883, n_α 1·52170, n_D 1·52692, n_β 1·54041, n_γ 1·55267 (at 21·7°).

4-*Benzyl*-1-*methyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadien*-4-*ol*, prepared in the same way from magnesium benzyl chloride, forms white needles, m. p. 94°, and yields *aa-dichloro-β-phenyl-β*-p-*tolylethane*, flat prisms, m. p. 94—95°, *a-phenyl-a*-p-*tolylethane*, b. p. 154—155·8°/14 mm., on reduction with sodium and alcohol, and *β-chloro-a-phenyl-4-methylstyrene*, m. p. 79—80°.

The crude product obtained by the action of magnesium *iso*propyl

bromide decomposes on being heated gradually to 160°, and then, on distillation, a large fraction, b. p. 141—143°/13 mm., and a smaller one, *, b. p. 160—180°/13 mm., may be obtained. The former is a mixture of dichlorides, one of which yields p-*tert*.-butyltoluene on reduction with sodium and moist ether (b. p. 190°, $D_4^{13\cdot25}$ 0·8667, n_α 1·49118, n_D 1·49465, n_β 1·50513, n_γ 1·51400, at 13·25°), whilst the other gives an *aldehyde*, probably 2- or 3-methyl-4-*iso*propylbenzaldehyde, when the crude mixture is dissolved in cold concentrated sulphuric acid. The aldehyde is a fragrant oil, b. p. 122—123°/14 mm., $D_4^{17\cdot4}$ 0·9813, n_α 1·53093, n_D 1·53628, n_β 1·55187, n_γ 1·56607, at 17·4°, undergoes oxidation to an *acid*, m. p. 91—92°, on exposure to the air, and forms a *semicarbazone*, in pearly leaflets, m. p. 206—209°.

It was anticipated that the dichloride would yield α-*p*-tolyl-α-methylpropaldehyde. This has been synthesised for comparison. *p*-Tolualdehyde is converted into *p*-methylmandelic acid, the *methyl* ester, m. p. 48—50°, is treated with magnesium methyl iodide, and so transformed into α-p-*tolyl*-β-*methylpropan*-αβ-*diol*, b. p. 168°/14 mm., m. p. 56·5—57·5°, and this is distilled with dilute sulphuric acid. α-p-*Tolyl*-α-*methylpropaldehyde* passes over as a pleasant smelling oil, b. p. 128—129°/24 mm., $D_4^{17\cdot4}$ 0·9706, n_α 1·50815, n_D 1·51204, n_β 1·52340, n_γ 1·53297, at 17·4°, which forms a *semicarbazone*, m. p. 172°, and an *oxime* m. p. 73—74°.

The above fraction * consists of 1-*methyl*-1-*dichloromethyl*-2-iso-*propyl*-Δ⁵-cyclo*hexen*-4-*one*. It crystallises in stout prisms, m. p. 84°, forms a *semicarbazone*, m. p. 191—196°, a p-*nitrophenylhydrazone*, m. p. 185°, two isomeric *oximes*, stout prisms, m. p. 120—121°, and flat needles, m. p. 139—141°, a *dibromide*, m. p. 139—141°, and a *benzylidene* compound, silky needles, m. p. 173°.

J. C. W.

Action of Alcoholic Potassium Hydroxide on Ketones. III. Action of Alcoholic Potassium Hydroxide on Halogeno-amino-benzophenones and -benzhydrols. P. J. MONTAGNE (*Ber.*, 1916, **49**, 2243—2262. Compare A., 1908, i, 988; 1913, i, 55).—The author continues his study of the influence of substituents on the reduction of benzophenones to benzhydrols by alcoholic potassium hydroxide and on the replaceability of halogen atoms in benzophenones. In the case of the bromobenzophenones, two reactions proceed simultaneously, but the speed of the one may be overwhelmingly greater than that of the other, according to the position of the halogen atom. Either bromine is eliminated and then the benzophenone is reduced to benzhydrol or the bromobenzophenone is reduced to bromobenzhydrol and nothing further takes place. Amino-groups have been shown to be a great hindrance to the reduction, and compounds containing both these and halogens have now been examined in order to find whether halogen atoms can counteract the effect of the amino-groups or amino-groups can prevent the elimination of halogen. Two halogen atoms in the para-positions will neutralise the influence of two amino-groups in the meta-positions.

The author believes that the time is now ripe for an exact quantitative re-examination of the whole problem.

p-Nitrobenzyl chloride condenses with chlorobenzene to form 2(?)-chloro-4′-nitrodiphenylmethane, m. p. 65°, b. p. 234°/17 mm., and 4-chloro-4′-nitrodiphenylmethane, m. p. 104·5°, b. p. 247°/19 mm. (compare Boeseken, A., 1904, i, 384), and the latter yields *4-chloro-4′-nitrobenzophenone* on oxidation with chromic acid. This crystallises in pale yellow, triclinic-pinacoidal needles [$a:b:c = 1·166:1:0·995$; $\alpha = 125°58'$, $\beta = 128°28'$, $\gamma = 68°22'$], m. p. 100·75°, b. p. 246°/12 mm., and may also be obtained from *p*-nitrobenzoyl chloride and chlorobenzene. The latter synthesis also gives rise to a small amount of *2(?)-chloro-4′-nitrobenzophenone*, which may likewise be prepared by oxidising the corresponding diphenylmethane derivative; it separates in large, lustrous, wine-yellow, rhombic-bipyramidal crystals [$a:b:c = 2·6857:1:1·7153$], m. p. 107·5°, b. p. 229°/10 mm., and may be reduced by means of stannous chloride to *2(?)-chloro-4′-aminobenzophenone*, in stout, pale yellow, monoclinic-prismatic crystals [$a:b:c = 0·5141:1:0·4824$; $\beta = 81°5'$], m. p. 112°. Similarly, *4-chloro-4′-aminobenzophenone* is readily obtained in pale crystals, m. p. 104·5°, b. p. 262°/14 mm. This does not suffer reduction on boiling with alcoholic potassium hydroxide, and only a trace of halogen is eliminated.

The bromo-compounds may be obtained in the same way. *2(?)-Bromo-4′-nitrobenzophenone* has m. p. 109·5°, b. p. 239°/10 mm., *4-bromo-4′-nitrobenzophenone* has m. p. 125°, b. p. 264°/16 mm., *4-bromo-4′-aminobenzophenone* has m. p. 196·5°, b. p. 279°/15 mm., and when boiled with alcoholic potassium hydroxide only suffers the loss of a trace of bromine.

3:3′-Diaminobenzophenone, m. p. 150—160°, b. p. 285°/11 mm., is partly reduced to the benzhydrol after boiling with alcoholic potassium hydroxide for two days. 4-Bromo-3:3′-diaminobenzophenone (following abstract) suffers loss of a considerable amount of bromine, but is mainly converted into *4-bromo-3:3′-diaminobenzhydrol*, m. p. 110·5°, which is quite stable towards the alkali. 4:4′-Dichloro-3:3′-diaminobenzophenone (A., 1915, i, 821) is almost completely reduced to *4:4′-dichloro-3:3′-diaminobenzhydrol*, m. p. 118·5°, whilst the dibromo-compound loses a fair amount of bromine and also yields *4:4′-dibromo-3:3′-diaminobenzhydrol*, m. p. 126°.

The m. p.'s and b. p.'s were determined with corrected thermometers. J. C. W.

Nitration of 4-Bromo- and 4-Chloro-benzophenones. P. J. MONTAGNE (*Ber.*, 1916, **49**, 2262—2276).—When 4-bromo- and 4-chloro-benzophenones are treated with pure nitric acid in the cold, they each give three dinitro-compounds. The purpose of the present communication is to show that the main product is the 4-halogeno-3:3′-dinitrobenzophenone, that the chief by-product is the 4-halogeno-3:2′-dinitro-compound, and that the substance which is produced in the smallest amount is the 4-halogeno-3:4′-dinitro-compound. The arguments also serve to demonstrate the

positions of the substituents in 4-halogeno-2′-, 3′-, and 4′-nitrobenzophenones.

When *o*-nitrobenzyl chloride is condensed with bromobenzene and the diphenylmethane derivative is oxidised with chromic acid, *4-bromo-2′-nitrobenzophenone* is produced, in crystals, m. p. 156°, b. p. 248°/11 mm. This yields *4-bromo-3 : 2′-dinitrobenzophenone*, m. p. 150°, when treated with pure nitric acid, and this is also formed as a by-product when 4-bromo-3-nitrobenzophenone is nitrated. *m*-Nitrobenzoyl chloride condenses with bromobenzene to form *4-bromo-3′-nitrobenzophenone*, m. p. 109·5°, b. p. 254°/11 mm., mixed with a little *2(?)-bromo-3′-nitrobenzophenone*, m. p. 81·5°, and when this 4-bromo-3′-nitro-compound is nitrated it yields *4-bromo-3 : 3′-dinitrobenzophenone*, m. p. 178°. On reduction with stannous chloride, this gives *4-bromo-3 : 3′-diaminobenzophenone*, m. p. 98—99°, which may be further reduced by sodium amalgam to 3 : 3′-diaminobenzhydrol. 4-Bromo-4′-nitrobenzophenone (preceding abstract) yields *4-bromo-3 : 4′-dinitrobenzophenone* on nitration, in very long, slender, pale yellow, rhombic-bipyramidal needles [$a:b:c = 1{\cdot}6350:1:1{\cdot}288$], m. p. 134·5°, and this may also be reduced to *4-bromo-3 : 4′-diaminobenzophenone*, m. p. 164°.

4-Chloro-2′-nitrobenzophenone, m. p. 151·5°, b. p. 236°/11 mm., from *o*-nitrobenzyl chloride and chlorobenzene, yields *4-chloro-3 : 2′-dinitrobenzophenone*, m. p. 123·5°, on nitration. *4-Chloro-3′-nitrobenzophenone*, m. p. 95·5°, b. p. 247°/13 mm., from *m*-nitrobenzoyl chloride and chlorobenzene, gives *4-chloro-3 : 3′-dinitrobenzophenone*, m. p. 166°. (A trace of *2(?)-chloro-3′-nitrobenzophenone*, m. p. 71·5°, is formed during the last Friedel-Crafts synthesis.) 4-Chloro-4′-nitrobenzophenone (preceding abstract) yields *4-chloro-3 : 4′-dinitrobenzophenone*, m. p. 137°, and this may be reduced to *4-chloro-3 : 4′-diaminobenzophenone*, m. p. 164·5° *3 : 4′-Diaminobenzhydrol*, m. p. 123·75°, is formed when either 3 : 4′-diaminobenzophenone itself or its 4-bromo- or 4-chloro-derivative is treated with sodium amalgam.

The isolation of the above dinitrobenzophenones from the mixtures obtained by nitrating 4-chloro- and 4-bromo-benzophenones is described.

4-Bromo-3-nitrobenzophenone, from 4-bromo-3-nitrobenzoyl chloride and benzene, crystallises in transparent, pale yellow, flat needles or rhombic-bipyramidal prisms [$a:b:c = 1{\cdot}5453:1:0{\cdot}3847$], m. p. 113·25°, b. p. 251°/16 mm., and yields 4-bromo-3 : 2′-dinitrobenzophenone on nitration. 4-Chloro-3-nitrobenzophenone (Maron and Fox, A., 1915, i, 265) forms pale yellow, rhombic-bipyramidal crystals [$a:b:c = 0{\cdot}9363:1:0{\cdot}5740$], m. p. 105·5°, b. p. 235°/13 mm., and yields 4-chloro-3 : 2′-dinitrobenzophenone on nitration.

J. C. W.

5- and 7-Hydroxyhydrindones. K. von Auwers and E Hilliger (*Ber.*, 1916, **49**, 2410—2413).—*Phenyl α-bromopropionate* is readily obtained by boiling phenol with α-bromopropionyl chloride, as a colourless oil, b. p. 135°/17 mm. When this is heated in small portions at a time with aluminium chloride at

140—150°, it gives good yields of 7-*hydroxy-α-hydrindone*, which is volatile in steam, and the para-compound, 5-*hydroxy-α-hydrindone*, $OH\cdot C_6H_3<{CH_2 \atop CO}>CH_2$, which crystallises in glistening prisms, m. p. 183°, and forms a *semicarbazone*, m. p. 223°. The ortho-compound was recently described by Knake and Salkowski as a product of the dehydration of β-*m*-hydroxyphenylpropionic acid, but they did not decide the position of the hydroxyl group (A., 1916, i, 820).

When attempts are made to treat large quantities of the above ester in this way, 1-methylcoumaranone is obtained in varying amounts, but this can be removed by a preliminary steam distillation from a strongly alkaline solution. J. C. W.

Naphthasultam. II. Naphthasultamquinone and its Derivatives, and Ketochlorides of Tetrahydronaphthasultam. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1916, **412**, 78—111. Compare A., 1916, i, 426).—The analogy between 1:8-naphthasultam and α-naphthol in their behaviour with chlorine (*loc. cit.*) also extends to the quinones and their derivatives and to the ketochlorides and phenazines.

4-*Amino*-1:8-*naphthasultam*, $NH_2\cdot C_{10}H_5<{SO_2 \atop NH}$, yellow needles, is obtained by reducing sodium 1:8-naphthasultam-4-azobenzenesulphonate, prepared in the usual way from naphthasultam and diazotised sulphanilic acid in alkaline solution, with dilute stannous chloride solution and treating the resulting *hydrochloride*, faintly yellow needles or leaflets with $1H_2O$, with aqueous sodium acetate. It forms a *diacetyl* derivative, colourless crystals, m. p. above 260° (which is easily hydrolysed to a *monoacetyl* derivative, colourless needles, m. p. 276°), and a *sulphate*, colourless crystals, which is oxidised by *N*-dichromate in the cold to 1:8-*naphthasultam*-4-*quinone*, $O:C_{10}H_5<{SO_2 \atop N}$, honey-yellow or slightly brown plates and leaflets. The quinone is odourless and has m. p. 195° (decomp.; blackening at 150°), and in general resembles α-naphthaquinone in its behaviour. It is reduced in alcoholic solution by stannous chloride to 4-*hydroxy*-1:8-*naphthasultam*, $C_{10}H_7O_3NS$, slightly yellow needles, blackening above 120° (*diacetyl* derivative, colourless needles, m. p. 199°), and reacts with aniline in the same solvent to form 3-*anilino*-1:8-*naphthasultam*-4-*quinone*,

$$C_{16}H_{10}O_3N_2S,$$

red needles, m. p. 257—260° (decomp.). The latter is converted, by heating with aqueous *N*/4-sodium hydroxide and acidifying, into 3-*hydroxynaphthasultamquinone*, $C_{10}H_5O_4NS$, yellow or faintly brown needles, m. p. about 230°, with previous sintering, which forms a *sodium* salt, red leaflets, does not yield an acetyl derivative, and is converted by aniline in warm alcoholic solution into the *aniline* salt, orange-red needles, in hot glacial acetic acid into the original anilino-compound. The hydroxynaphthasultamquinone is reduced by hot aqueous stannous chloride to 3:4-*dihydroxy*-1:8-

naphthasultam, $C_{10}H_7O_4NS$, faintly yellow needles, m. p. about 230°, with previous blackening (*triacetyl* derivative, colourless leaflets, m. p. 222°), and reacts with *o*-phenylenediamine in hot alcohol to form 1 : 8-*naphthasultam*-3 : 4-*phenazine*, $C_6H_4<\genfrac{}{}{0pt}{}{N}{N}>C_{10}H_4<\genfrac{}{}{0pt}{}{SO_2}{NH}$, dark red needles, m. p. above 260° (decomp.), which is amphoteric; the *sodium* salt and the *hydrochloride*, brownish-yellow needles, have been prepared, and the *acetyl* derivative forms faintly yellow needles, m. p. about 270°.

2-*Chloro*-1 : 8-*naphthasultam* - 4 - *quinone*, $C_{10}H_4O_3NClS$, yellow leaflets, m. p. 217—218°, prepared by oxidising 2 : 4-dichloro-1 : 8-naphthasultam (*loc. cit.*) with hot nitric acid, D 1·32, is reduced to 2-*chloro*-4-*hydroxy*-1 : 8-*naphthasultam*, faintly yellow needles, m. p. about 250° (decomp.; blackening at 230°) (*acetyl* derivative, colourless needles, m. p. 186°), by stannous chloride and hot glacial acetic acid, and reacts with aniline in the same solvent to form 2-chloro-3-anilinonaphthasultamquinone (*loc. cit.*).

2 : 3 : 4-Trichloro-1 : 8-naphthasultam (*loc. cit.*) suspended in glacial acetic acid is oxidised by nitric acid, D 1·4, on the water-bath to 2 : 3-*dichloro*-1 : 8-*naphthasultam*-4-*quinone*, $C_{10}H_3O_3NCl_2S$, yellow needles, m. p. 216—217°, which is also easily obtained from 4-aminonaphthasultam in the manner described below. The dichloroquinone, which shows a great similarity in behaviour to 2 : 3 - dichloro-α-naphthaquinone, yields 2-chloro-3-anilinonaphthasultamquinone by treatment with aniline in glacial acetic acid, is reduced by stannous chloride to 2 : 3-*dichloro*-4-*hydroxy*-1 : 8-*naphthasultam*, $C_{10}H_5O_3NCl_2S$, almost colourless needles, m. p. about 254°, after darkening at 220° (*sodium* salt, yellow crystals; *diacetyl* derivative, colourless needles, m. p. 205—206°), yields 2-*chloro*-1 : 8-*naphthasultam*-3 : 4-*phenazine*, $C_{16}H_8O_2N_3ClS$, reddish-brown needles with a bronze lustre, decomp. above 290°, by treatment with *o*-phenylenediamine in boiling alcohol, and is converted by 2*N*-sodium hydroxide into 2-*chloro*-3-*hydroxy*-1 : 8-*naphthasultam*-4-*quinone*, $C_{10}H_4O_4NClS$, yellow needles or prisms, which exhibits the curious property of dissolving in water or alcohol with a deep red colour, being reprecipitated unchanged by hydrochloric or nitric acid. The last-named compound is also converted into the preceding phenazine by *o*-phenylenediamine, and is reduced by stannous chloride solution and boiling glacial acetic acid to 2-*chloro*-3 : 4-*dihydroxy*-1 : 8-*naphthasultam*, $C_{10}H_6O_4NClS$, faintly yellow needles, m. p. about 256° with previous blackening, which forms a *diacetyl* derivative, colourless needles, m. p. about 285° (decomp.).

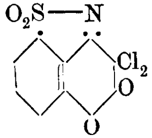
2 : 2 : 3 : 3-*Tetrachloro*-1 : 8-*naphthasultam*-4-*quinone*,

$$O:C_{10}H_3Cl_4<\genfrac{}{}{0pt}{}{SO_2}{N},$$

m. p. 175°, colourless leaflets or plates containing $1H_2O$, can be prepared from naphthasultamquinone or 2 : 3-dichloronaphthasultamquinone by moderated chlorination, but is best obtained by saturating with chlorine a suspension of 4-aminonaphthasultam

hydrochloride in glacial acetic and concentrated hydrochloric acids. It liberates iodine from acidified potassium iodide, yields 2 : 3-dichloro-4-hydroxy-1 : 8-naphthasultam by reduction, and is decomposed by alkali, extensively in warm aqueous solution, but in cold aqueous alcoholic solution yielding an *acid*, slender needles, which probably has the formula $CO_2H\cdot C_6H_3<{SO_2\cdot N \atop \text{——}C}\cdot CCl{:}CCl_2$.

2 : 2-*Dichloro*-3-*keto*-1 : 8-*naphthasultam*-4-*quinone* (annexed formula), m. p. 195—196° (decomp.), almost colourless needles or faintly yellow plates with $2H_2O$, is obtained by chlorinating 2-chloro-3-hydroxy-1 : 8-naphthasultam-4-quinone in chloroform or glacial acetic acid. It yields chlorohydroxynaphthasultamquinone or chlorodihydroxynaphthasultam by reduction, is decomposed by boiling water or alkalis, and reacts with *o*-phenylenediamine in cold glacial acetic acid to form the 3 : 4-*phenazine*, $C_{16}H_7O_2N_3Cl_2S$, faintly red needles, m. p. 265—266° (decomp.). The formation of this azine not only shows the presence of two ortho keto-groups, but is evidence of the constitution of 2-chloro-3-hydroxy-1 : 8-naphthasultamquinone, and furnishes a further proof of the constitution of 3-hydroxynaphthasultamquinone and the corresponding anilino-derivative. The azine is converted by stannous chloride and glacial acetic acid into 2-chloronaphthasultam-3 : 4-phenazine, a suspension of which in glacial acetic acid is oxidised by warming carefully with nitric acid, D 1·4, to 2-*ketodihydronaphthasultam*-3 : 4-*phenazine*,



$$C_6H_4<{N \atop N}>C_{10}H_3O<{SO_2 \atop N},$$

yellowish-red leaflets or needles, m. p. above 280° (decomp.). This substance is reduced by stannous chloride and hot glacial acetic acid to 2-*hydroxy*-1 : 8-*naphthasultam*-3 : 4-*phenazine*, $C_{16}H_9O_3N_3S$, dirty green plates, m. p. above 270° (decomp.), which forms a *diacetyl* derivative, yellow needles, m. p. about 245—246°, with previous sintering. C. S.

Preparation of Bromo-α-hydroxyanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293694; from *J. Soc. Chem. Ind.*, 1916, **35**, 1149).—Bromo-derivatives of α-hydroxyanthraquinones, difficult to prepare in other ways, can be obtained by the action of bromine in presence of substances capable of combining with hydrogen bromide. Thus, α-hydroxyanthraquinone yields 4-bromo-α-hydroxyanthraquinone, m. p. 197—198°, anthrarufin gives 4 : 8-dibromo-1 : 5-dihydroxyanthraquinone, and chrysazin yields 2 : 4 : 5 : 7-tetrabromo-1 : 8-dihydroxyanthraquinone. H. W.

Preparation of Transformation Products of ω-Dibromo-2-*p*-toluoylbenzoic Acid, for example, Anthraquinone-2-aldehyde. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P. 293981; from *J. Soc. Chem. Ind.*, 1916, **35**, 1149).—Anthra-

quinone-2-aldehyde is obtained by heating ω-dibromo-2-*p*-toluoylbenzoic acid at a high temperature, or 4-aldehydobenzophenone-2′-carboxylic acid may be first formed by heating with sulphuric acid at a relatively low temperature and the action then completed at a higher temperature. Hydrolysing agents other than sulphuric acid, such as a dilute alkali solution, may be used for the first stage of the process, and any suitable dehydrating agent for the second stage. H. W.

Preparation of Dianthraquinonylene Dioxides. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P., 293660; from *J. Soc. Chem. Ind.*, 1916, **35**, 1151).—*o*-Nitrohydroxyanthraquinones are heated with alkaline condensing agents at a high temperature. The products, which are formed by the union of two molecules of the anthraquinone derivative with elimination of two molecules of nitrous acid, are either vat dyes or may be used in the manufacture of dyes. H. W.

The Chemistry of the Saponins. A. W. van der Haar (*Biochem. Zeitsch.*, 1916, **76**, 335—349).—The author gives a summary of his investigations (without experimental details) on the chemistry of the saponins of *Polyscia*, the crystalline α-hederin of ivy, and of saponaria- and aralea-saponins, and of senegin and digitonin. The polyscia-saponin gives on hydrolysis with 5% sulphuric acid about 33% arabinose, 37·6% dextrose, and 35% sapogenin. The latter forms rhombic crystals, m. p. 324°, contains a lactone group, but no carboxyl, hydroxyl, or methoxyl group. It has the formula $C_{26}H_{44}O_4$.

A method is indicated (without details) for the preparation of α-hederin, m. p. 256—257°, the crystalline saponin of ivy, which is insoluble in water. This substance, $C_{42}H_{66}O_{11}$, undergoes hydrolysis into the sapogenin (α-hydragenin) and arabinose and rhamnose, according to the equation $C_{42}H_{66}O_{11} + 3H_2O = C_{31}H_{50}O_4 + C_5H_{10}O_5 + C_6H_{12}O_5$. α-Hydragenin is crystalline, m. p. 325—326°, and contains a lactone and two hydroxyl groups. The same sapogenin is obtained from other saponins from ivy, which do not, however, yield the same sugars with α-hydragenin on hydrolysis. Many of the sapogenins yield on distillation with zinc dust in an atmosphere of hydrogen terpene hydrocarbons, to which the colour reaction of saponins with sulphuric acid is due. S. B. S.

Molecular Weight of Aloin and its Products of Oxidation. E. Seel and C. Kelber (*Ber.*, 1916, **49**, 2364—2368).—The following mean values for the molecular weight of aloin are recorded: cryoscopic method: phenol, 197; ebullioscopic method: acetone, 408; ethyl alcohol, 440; ethyl acetate or acetic acid, no increment at all. These values support Léger's view that aloin has the formula $C_{21}H_{20}O_9$ or $C_{20}H_{18}O_9$ rather than $C_{16}H_{18}O_7$, which was previously assumed to be correct. Léger obtained an anthraquinone derivative and a sugar on hydrolysis (A., 1910, i, 463),

and Seel also obtained a methyltetrahydroxyanthraquinone by oxidising aloin (A., 1901, i, 92). This gives the expected increment with boiling ethylene dibromide, and the tetra-acetate causes the expected depression in the freezing point of benzene.

J. C. W.

Anthocyanins. XI. The Anthocyanin of Red-flowering Varieties of Salvia. R. WILLSTÄTTER and E. K. BOLTON (*Annalen*, 1916, **412**, 113—136).—As the investigation of the colouring matters of flowers extends, it becomes more and more evident that only a small number of sugar-free colouring matters occur in the anthocyanins, the almost infinite diversity of colour of flowers being due partly to the more or less extensive methylation of, chiefly to the nature, number, and method of union of the sugar molecules combined with, pelargonidin, cyanidin, and delphinidin (compare A., 1915, i, 282).

The scarlet-red flowers of *Salvia coccinea* and *S. splendens* contain an anthocyanin, called *salvianin*, which is a glucoside of pelargonidin, but differs in properties and behaviour from any of the known pelargonidin derivatives. The flowers are digested with ten times the weight of glacial acetic acid, and, after several days, the filtered extract is treated with ether, whereby a crude acetate is obtained, after drying, as a purplish-red powder. This is dissolved in 0·05% hydrochloric acid and treated with a saturated solution of picric acid. The crude picrate thus obtained, in amorphous, brownish-red flocks, is converted by methyl-alcoholic hydrogen chloride and ether into *salvianin chloride*, a scarlet-red powder. All attempts to prepare the chloride directly yielded only oily products. By shaking the crude anthocyanin, dissolved in about 3·5% hydrochloric acid, with a large quantity of amyl alcohol, the organic solvent removes a small amount of the anthocyanin, and from this *salvianin picrate* has been obtained in very slender, brownish-red, metallic needles. The bulk of the anthocyanin is removed from the acid mother liquor by propyl alcohol, but the picrate prepared therefrom is amorphous.

Salvianin has a complex composition and is not a simple diglucoside, since it yields by hydrolysis with boiling 20% hydrochloric acid not only pelargonidin and 2 mols. of dextrose, but also malonic acid in considerable quantity.

By keeping its solution in 6% hydrochloric acid over concentrated hydrochloric acid (renewed from time to time) in a desiccator for weeks or months, salvianin is slowly changed into a normal diglucoside, *salvinin*, and a compound, *salvin*, intermediate between this and salvianin. Salvinin forms a *chloride*, $C_{27}H_{31}O_{15}Cl$, m. p. 168° (decomp.), needles with $5H_2O$, and is isomeric with and very similar to pelargonin, but differs from it in several ways, particularly in the much stronger fluorescence of the alcoholic solution of its chloride. By hydrolysis with boiling 10—20% hydrochloric acid, salvinin yields pelargonidin and dextrose (2 mols.), but the solution obtained after the hydrolysis has proceeded for ten to twenty seconds indicates, by its colour

and its partition with amyl alcohol, the presence of an intermediate, monoglucosidic product of hydrolysis. The isolation of salvianin in quantity from the flowers is attended with not inconsiderable difficulties, and therefore the investigation of the preceding monoglucoside has not yet been attempted. However, pelargonin behaves in a similar manner, and by hydrolysis with boiling 20% hydrochloric acid for twenty to forty seconds yields a monoglucoside, *pelargonenin* (which does not appear to be identical with that from salvinin), the *chloride* of which, $C_{21}H_{21}O_{10}Cl$, forms scarlet-red needles with $2H_2O$, and is much more intensely fluorescent in alcoholic solution than is pelargonin chloride.

Salvin has not yet been fully investigated, but it appears to be different from salvianin. Its *chloride*, $C_{27}H_{27}O_{13}Cl$ (?), forms dark red prisms (from which only an oily picrate could be obtained); it is less fluorescent, and its solutions in alkalis are less blue than those of salvianin. The analytical data indicate that salvin is $C_{27}H_{26}O_{13}$ (that is, a pelargonin $-2H_2O$), and from this it would appear that two molecules, not of dextrose, but of a derivative, $C_6H_{10}O_5$, thereof, are present in the compound. Salvin exhibits a peculiarity in its partition between dilute hydrochloric acid and amyl alcohol; whilst solutions of all the diglucosides as yet examined (except rhamnoglucosides, which approximate to the monoglucosides in their behaviour) yield only a few units per cent. of their colouring matter to amyl alcohol, solutions of salvin yield more than 50% (salvianin yields almost exactly 50%). C. S.

Anthocyanins. XII. Anthocyanin of the Winter Aster (Chrysanthemum). R. WILLSTÄTTER and E. K. BOLTON (*Annalen*, 1916, **412**, 136—148).—A large number of scarlet-red, red, and dark red varieties of *Chrysanthemum indicum*, L., are found to contain the same cyanidin monoglucoside, which is called *chrysanthemin*, mixed in many cases with carotin and xanthophyll; in particular, the dried florets of the dark red Ruby King contain about 7% of chrysanthemin. The florets are digested for three days with glacial acetic acid (15 parts), and the chrysanthemin is precipitated by ether as the acetate, a dark violet-red powder. A solution of this in 0·5% hydrochloric acid is shaken twice with amyl alcohol and treated with a cold saturated solution of picric acid; the resulting impure picrate is converted by 10% methyl-alcoholic hydrogen chloride and ether into the impure chloride, a brownish-red, amorphous powder, and the latter is obtained in the pure, crystalline state by repeated separation from aqueous alcoholic hydrochloric acid. An alternative method of purification, based on the characteristic partition of a monoglucoside between dilute mineral acid and amyl alcohol, showed that the crude acetate obtained above contained some cyanidin and a diglucoside which is very nearly related to, if it is not identical with, cyanin.

Chrysanthemin chloride, $C_{21}H_{21}O_{11}Cl$, crystallises in clusters of acute-angled rhombic leaflets which exhibit a magnificent metallic

lustre, and are greyish-violet by transmitted light; the powder is Bordeaux-red. The substance begins to decompose at 205° and blackens without melting. It yields cyanidin chloride and dextrose (1 mol.) by hydrolysis with boiling hydrochloric acid. The *picrate* forms thin, red prisms, m. p. 165° (decomp.), sintering at 155°.

Chrysanthemin resembles the isomeric galactoside idaein in its reactions. It is also very similar to asterin (following abstract). Both these cyanidin monoglucosides exhibit the same intense ferric chloride reaction as cyanin, but differ from it in giving a violet instead of a cornflower-blue coloration with aqueous sodium carbonate.

The extraordinary dissemination of cyanidin among the anthocyanins, very frequently in the form of diglucosides, less frequently, but still not uncommonly, in the form of monoglucosides, becomes increasingly evident. Cyanin or a very similar cyanidin glucoside has often been isolated from scarlet flowers in which the presence of pelargonidin glucosides would have been expected. *Zinnia elegans* (Jacq.), *Gaillardia bicolor* (Hook), *Helenium autumnale*, L., *Gladiolus* (the scarlet varieties of which contain a pelargonidin glucoside), *Tulipa Gesneriana*, L., *Tropaeolum majus*, L., *Ribes rubrum*, L., the raspberry, and the berry of the mountain ash contain cyanidin glucosides in larger or smaller quantities, together with carotin, xanthophyll, and other pigments.

C. S.

Anthocyanins. XIII. Two Anthocyanins of the Summer Aster. R. WILLSTÄTTER and CH. L. BURDICK (*Annalen*, 1916, **412**, 149—164).—The dried florets of the purplish-red summer (china) aster (*Callistephus Chinensis*, Nees, syn. *Aster Chinensis*, L.) contain about 7·4% of a mixture of two monoglucosidic anthocyanins; the one occurring in predominant quantity is named *asterin*, the other *callistephin*.

The undried flowers were cut up and, owing to uncontrollable circumstances connected with the outbreak of the war, were digested with glacial acetic acid for a month, whereby a large part of the colouring matter in the extract was spoilt and the purification was rendered much more difficult than would have been the case had the extraction been rapidly effected. Two methods of purification are described, one involving the use of propyl alcohol and the formation of the picrates, the other utilising the lead salts. The latter, which is the better method, is as follows: The syrupy, hygroscopic mass precipitated from the acetic acid extract by ether is dissolved in 0·01% hydrochloric acid and the filtered solution is treated with lead acetate. The blue precipitate of lead salts (of the anthocyanins and of impurities) is at once extracted with glacial acetic acid, whereby a large portion of the impurities is undissolved, and the lead salts in the extract are precipitated by ether. The precipitate is shaken with propyl alcohol and 25% methyl-alcoholic hydrogen chloride, and the filtered extract is treated with ether to precipitate the chlorides of the two antho-

cyanins. These are still too impure to yield crystalline picrates, and therefore the whole process of purification is repeated. The amorphous chlorides now obtained are dissolved in 0·5% methyl-alcoholic hydrogen chloride and the filtered solution is treated with 7% hydrochloric acid and kept for five days, evaporation of methyl alcohol not being checked. The chloride which separates is submitted twice to a repetition of the process, 0·25% methyl-alcoholic hydrogen chloride being used, and pure asterin chloride is thereby obtained. Callistephin chloride is obtained by treating the mother liquors with alcohol and ether, dissolving the precipitate in methyl alcohol, and adding about 10% hydrochloric acid.

Asterin chloride, $C_{21}H_{21}O_{11}Cl$, forms bronze-brown or reddish-brown, metallic, stout prisms containing $1\frac{1}{2}H_2O$. It gives the same violet coloration with sodium carbonate and the same blue coloration with alcoholic ferric chloride as does chrysanthemin chloride (preceding abstract), but differs from this isomeric monoglucoside in being easily soluble in alcohol and in 0·5% hydrochloric acid. By hydrolysis with boiling 20% hydrochloric acid, asterin yields cyanidin and dextrose (1 mol.).

Callistephin chloride, $C_{21}H_{21}O_{10}Cl$, forms a dark brownish-red, bronze mass of hair-like needles, which appear orange-yellow under the microscope. The crystals contain $2—2\frac{1}{2}H_2O$. Although isomeric with pelargonenin (Willstätter and Bolton, this vol., i, 43), callistephin differs from it in giving a reddish-violet solution in alkalis, in forming a yellowish-red, non-fluorescent solution in alcohol, and particularly in being very easily soluble in hydrochloric acid even up to 7% concentration. Callistephin does not react with alcoholic ferric chloride, and it yields pelargonidin and dextrose (1 mol.) by hydrolysis. C. S.

Anthocyanins. XIV. Colouring Matter of the Cherry and of the Sloe. R. Willstätter and Ernst H. Zollinger (*Annalen*, 1916, **412**, 164—178).—Cyanidin glucosides occur very extensively in fruits, in yellowish-red, red, brown, and dark blue berries. Allied to idaein of the cranberry (Willstätter and Mallison, A., 1915, i, 282), *keracyanin* has been isolated from the cherry (*Prunus avium*) and *prunicyanin* from the sloe (*Prunus spinosa*). The plum (*Prunus domestica*) also contains a cyanidin glucoside, and the authors direct attention to the occurrence of a pure red colouring matter in the bluish-black skins of such fruits, and state that some explanation must be found as to how cyanidin is able to impart such deep colours to fruits.

The extraction of anthocyanins from fruit skins is comparatively simple. The dark reddish-brown skins of the cherry are separated from the rest of the fruit, freed completely from pulp by hydraulic pressure, and are extracted with glacial acetic acid without delay. The syrupy deposit obtained from the extract by the addition of ether is freed from a considerable quantity of colourless impurities by 0·5% methyl-alcoholic hydrogen chloride and ether, the solution is treated with an excess of lead acetate, the precipitated lead salts are extracted with glacial acetic acid, the extract (containing the

colouring matters, colourless impurities not being dissolved when the amount of acetic acid is suitably selected) is again precipitated with lead acetate or with ether, and the precipitate is dissolved in methyl-alcoholic hydrogen chloride. The crude chloride precipitated from the last solution by ether is purified by fractional precipitation of its solution in 0·1% methyl-alcoholic hydrogen chloride by ether. *Keracyanin chloride*, $C_{27}H_{31}O_{15}Cl$, forms red clusters of very slender needles containing $4H_2O$ (these appear yellow under the microscope), or stout prisms containing $3H_2O$ (brownish-yellow under the microscope). It resembles cyanin in the colour of its solutions in mineral acids and alcohol, but differs in giving a reddish-violet coloration in aqueous sodium carbonate and in being more soluble in dilute acids, ethyl alcohol, and amyl alcohol.

Keracyanin is a diglucoside, and by hydrolysis with boiling 20% hydrochloric acid for two and a-half to three minutes yields cyanidin, dextrose, and rhamnose.

Keracyanin and prunicyanin (see below) exhibit an important difference from other diglucosides in their partition between dilute mineral acid and amyl alcohol. Whilst cyanin and similar diglucosides yield only 1—2% of the anthocyanin to the organic solvent, keracyanin and prunicyanin resemble monoglucosides in yielding nearly 10%.

The extraction of *prunicyanin* from the skins of sloes by glacial acetic acid, the precipitation of a red syrup by methyl-alcoholic hydrogen chloride and ether, and the several processes required for the further purification of the anthocyanin are described somewhat briefly. *Prunicyanin chloride* does not crystallise readily, and therefore has not been isolated free from ash. It dissolves very easily in dilute or concentrated hydrochloric acid, develops a bluish-violet coloration with aqueous sodium carbonate, and pure blue with alcoholic ferric chloride, and yields cyanidin, rhamnose, and a hexose by hydrolysis.

Prunicyanin is comparable in many respects with mecocyanin (Willstätter and Weil, following abstract). C. S.

Anthocyanins. XV. Anthocyanin of the Pansy. R. Willstätter and Friedrich Josef Weil (*Annalen*, 1916, **412**, 178—194).—Glucosides of delphinidin mono- and di-methyl ethers occur extensively in flowers and fruits, but a sugar-compound of delphinidin itself has hitherto only been found in delphinin, the anthocyanin of the larkspur (Willstätter and Mieg, A., 1915, i, 284). Since delphinin is not merely a glucoside, but yields also *p*-hydroxybenzoic acid by hydrolysis, the authors have investigated a number of blue and violet flowers with the object of finding a simple delphinidin glucoside corresponding with cyanin and pelargonin. The majority of these contained methylated delphinidins, but the flowers of the deep bluish-violet pansy (*Viola tricolor*) were found to contain a glucoside of delphinidin itself, which is called *violanin*. The dried flowers contain not less than 33% of the anthocyanin, calculated as the air-dried chloride.

The extract obtained by digesting the freshly gathered petals

with glacial acetic acid for fourteen days is treated with 10% methyl-alcoholic hydrogen chloride and ether, the precipitate is collected, washed with ether, dissolved in acidified water, and the filtered solution is treated with 4% hydrochloric acid, whereby pure *violanin chloride* is obtained. A remarkably pure crude product is obtained by rapidly extracting the flowers with 2% methyl-alcoholic hydrogen chloride and treating the filtered extract with ether. Violanin chloride forms bluish-violet aggregates of crystals with a green, metallic lustre; by careful crystallisation, six-sided and tetrahedral plates can be obtained. Violanin resembles delphinin in the colour of its solutions, but differs therefrom in forming a colourless carbinol (ψ-base) in dilute solution (*loc. cit.*). It forms pure blue solutions in alkali hydroxide or carbonate solutions, in disodium hydrogen phosphate solution, and with alcoholic ferric chloride or alum. By hydrolysis with boiling 20% hydrochloric acid, violanin chloride yields delphinidin, rhamnose, and dextrose, but the latter two are not obtained in molecular quantities. On this account the composition of violanin has not yet been definitely settled; it appears to be $C_{27}H_{28}O_{15}$, that is, delphinidin rhamnoglucoside, ($C_{27}H_{30}O_{16} - 1H_2O$).

Similarly to the other rhamnoglucosides, keracyanin and prunicyanin (preceding abstract), violanin resembles a monoglucoside in its partition between dilute acid and amyl alcohol. Fractional extraction with amyl alcohol proved that violanin is not a mixture of two or more constituents.

Violanin picrate forms cherry-red, felted needles which appear blue under the microscope; when dried, it forms a copper-red mass with a metallic lustre.

The identification of delphinidin and its purification are made somewhat difficult owing to its tendency to form hydrates of different appearance and widely varying solubility. Four of these, with 1, 1½, 2, and $4H_2O$ respectively, are described, and the conditions for their preparation given in detail. C. S.

Anthocyanins. XVI. Colouring Matter of the Grape and of the Bilberry. II. R. WILLSTÄTTER and ERNST H. ZOLLINGER (*Annalen*, 1916, **412**, 195—216. Compare A., 1915, i, 285).—The sugar present in myrtillin has been recognised as galactose (phenylmethylhydrazone, m. p. 188—189°). Myrtillidin yields phloroglucinol when it is heated with 75% potassium hydroxide at 110° for a few minutes. This fact, taken in conjunction with the intense ferric chloride reaction of myrtillidin, shows that the anthocyanidin (which is a delphinidin monomethyl ether) must have its methoxyl group in position 3 or 3′.

Grapes from different sources are shown in the following way to contain, in addition to the monoglucoside oenin, more or less of the sugar-free anthocyanidin, oenidin; it is very probable that a few units per cent. of a diglucoside are also present in some varieties of grapes. The grapes are pressed, and the skins, after being soaked in boiling water for a short time, are ground with sand and rapidly extracted with dilute aqueous hydrochloric acid.

The extract is shaken with amyl alcohol. The alcoholic solution, even after repeated washing with dilute acid, retains a small (in some cases a considerable) amount of colouring matter, which must therefore be the anthocyanidin. This is the case with grapes from North Italy, and also with indigenous greenhouse grapes.

The partition of anthocyanins between dilute mineral acid and amyl alcohol free from pyridine is of great analytical importance, not only for the preceding reason, the testing of the individuality of an anthocyanin, but also because it indicates whether an anthocyanin is a monoglucoside or a diglucoside. The acid must be sufficiently concentrated to prevent conversion of the coloured chloride into the colourless carbinol, and yet must be dilute enough to dissolve the chloride readily. The authors recommend 0·5% hydrochloric acid. The solutions in this solvent must be very dilute on account of the limited solubility of the colouring matter in amyl alcohol. The intensity of the colour of the amyl-alcoholic solution is compared with that of a freshly prepared, standard solution of the anthocyanin chloride. Two successive extractions with amyl alcohol are made, and the fraction of the anthocyanin in the extracts (called the "partition number") should be the same in both cases. By employing this method, the authors have prepared pure oenin chloride from Italian grapes. It forms dark prisms with a green metallic lustre, containing $4H_2O$ (compare *loc. cit.*).

The effect of tannins on the colour reactions of certain anthocyanins (cyanin, oenin, and myrtillin) is described.

The anthocyanin in the berries of the wild vine (*Ampelopsis quinquefolia* Michx.; *Vitis hederacea* Ehrh.) is present mainly in the skins, although not so completely as in the case of the cultivated vine. The skins are pressed between filter-paper and extracted with glacial acetic acid. The violet powder precipitated from the extract by ether is dissolved in methyl-alcoholic hydrogen chloride, and the crude chloride thrown out by ether is dissolved in 0·1% hydrochloric acid, and powdered picric acid is added to the solution. The *picrate* of the anthocyanin, which is called *ampelopsin*, is obtained in crimson red, felted needles. The picrate is converted by 3—4% methyl-alcoholic hydrogen chloride and ether into the nearly pure, amorphous chloride, which is obtained crystalline by further purification by aqueous-alcoholic hydrochloric acid. *Ampelopsin chloride*, $C_{22}H_{23}O_{12}Cl$, crystallises in dark brownish-green, glistening prisms resembling those of oenin chloride, and yields dextrose (1 mol.) and *ampelopsidin* by hydrolysis with boiling 20% hydrochloric acid.

The skins of the berries of *Vitis riparia*, treated in the manner described above, yield a crystalline monoglucosidic *anthocyanin chloride*, $C_{22}H_{23}O_{12}Cl$ (to which a specific name has not yet been given). This anthocyanin differs from ampelopsin in giving a pronounced, but transient, violet coloration with aqueous ferric chloride and a stable blue solution with alcoholic ferric chloride; ampelopsin develops a faint coloration with the former reagent and a fine violet with the latter. C. S.

Anthocyanins. XVII. The Colouring Matter of the Petunia. R. WILLSTÄTTER and CH. L. BURDICK (*Annalen*, 1916, **412**, 217—230).—The widely cultivated "Karlsruher Rathaus" petunia (*P. hybrida hort.*) contains an individual, well-crystallised anthocyanin, *petunin*, which is a diglucoside of *petunidin*, a new delphinidin monomethyl ether similar to myrtillidin. The flowers, which in the dried state contain 15·4% of hydrated petunin chloride, are rapidly extracted with glacial acetic acid; the purification by means of ether, methyl-alcoholic hydrogen chloride, etc., follows very much along the usual lines. *Petunin chloride*, $C_{28}H_{33}O_{17}Cl$, forms elongated plates containing $2H_2O$, m. p. about 178°, which appear a magnificent violet colour by transmitted light and have a copper lustre by reflected light. Its dilute aqueous solution loses its reddish-violet colour in the course of time, and then contains the colourless ψ-base. Petunin chloride is very easily soluble in methyl alcohol, develops a violet coloration with methyl-alcoholic (not ethyl-alcoholic) ferric chloride, and yields with aqueous sodium carbonate a solution the violet colour of which soon becomes blue.

Petunin is not precipitated as the picrate by picric acid.

By boiling with 20% hydrochloric acid, petunin chloride yields dextrose (2 mols.) and *petunidin chloride*, $C_{16}H_{13}O_7Cl$, which yields several hydrates having different crystalline forms and solubility. Petunidin closely resembles myrtillidin in its reactions, but shows the following two characteristic differences. Petunidin which has been washed with alcohol is insoluble in 0·5% hydrochloric acid, whilst myrtillidin after similar treatment is easily soluble. Petunidin crystallised from hydrochloric acid is insoluble in 3% hydrochloric acid, whilst myrtillidin is appreciably soluble.

Petunidin yields delphinidin by demethylation with hydriodic acid in the presence of phenol, and phloroglucinol by heating with very concentrated aqueous potassium hydroxide at 140°. C. S.

Anthocyanins. XVIII. Colouring Matter of the Poppy. I. R. WILLSTÄTTER and FRIEDRICH WEIL (*Annalen*, 1916, **412**, 231—251).—An investigation of the colouring matters of various kinds of poppy has been undertaken since preliminary experiments have indicated that the isolation of several new anthocyanidins (fundamental substances different from cyanidin, pelargonidin, and delphinidin) may be expected. At present, owing to the war, only one investigation has been finished, and this has not produced a new anthocyanidin.

The flowers of the corn-poppy (*Papaver Rhoeas*) contain a mixture of the diglucosides of two anthocyanidins. The predominating anthocyanin is a cyanidin derivative, and is named *mecocyanin*. The other anthocyanin resembles the delphinidin glucosides, but the anthocyanidin in it has not been obtained in the pure state.

The freshly gathered flowers are treated with glacial acetic acid, and the extract is treated with 10% methyl-alcoholic hydrogen chloride and ether. The product is further purified (1) by pre-

cipitation from hydrochloric acid solution by alcohol to remove slimy impurities; (2) solution in alcohol to remove the accompanying anthocyanin and inorganic salts; (3) separation from the alcoholic solution to remove the more easily soluble, less pure portions; and (4) fractional precipitation by glacial acetic acid from aqueous solution containing hydrochloric acid.

Mecocyanin chloride, $C_{27}H_{31}O_{16}Cl$, is obtained by the last operation in dark red, crystalline grains. It is easily soluble in water; the dilute solution becomes colourless owing to carbinol formation. It differs from cyanin and other cyanidin glucosides in its extreme solubility in hydrochloric acid (0·01% to 10% or more). Mecocyanin resembles cyanin in the colours of its solutions in acids and in alcohol, but differs in giving a bluish-violet solution in aqueous sodium carbonate. The salts of mecocyanin are very soluble except the *ferrocyanide*, which crystallises in almost black, felted needles with a green, metallic lustre.

Mecocyanin yields cyanidin chloride and dextrose (2 mols.) by hydrolysis with boiling 20% hydrochloric acid. By digesting mecocyanin with concentrated hydrochloric acid for a few hours or with 20% hydrochloric acid for a few days at the ordinary temperature, it is converted into a monoglucoside which is shown to be identical with chrysanthemin (Willstätter and Bolton, this vol., i, 43). C. S.

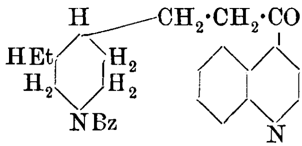
Preparation of α-Methylcoumarones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 293956; from *J. Soc. Chem, Ind.*, 1916, **35**, 1180; addition to D.R.-P., 279864, A., 1915, i, 707).—α-Methylcoumarones, suitable for pharmaceutical purposes and for use in perfumery, are formed by the action of alkalis on α-halogeno-*o*-allylphenols. H. W.

Degradation of the Cinchona-alkaloids. I. ADOLF KAUFMANN, ERNST ROTHLIN, and PAUL BRUNNSCHWEILER (*Ber.*, 1916, **49**, 2299—2310).—Recent researches have shown that meroquinenine or the product of its hydrogenation, cincholeupone, are common to all the cinchona-alkaloids, being combined in these with cinchonic or quinic acids. Derivatives of the latter acids are now easily prepared, and therefore if the former acids could be isolated readily from the less valuable alkaloids it might be possible to synthesise from them the more important bases. The difficulty has so far been the production of meroquinenine or cincholeupone in quantity, but improved methods are now described.

Starting with cinchotine, which can be obtained in large amounts by hydrogenating the vinyl chain in cinchonine, this is transformed by treatment with acetic acid into cinchotoxine; the benzoyl derivative of this is converted into the oximino-compound, and this is broken down by means of *p*-toluenesulphonyl chloride into cinchonic acid and benzoylcincholeupononitrile, which yields cincholeupone on hydrolysis. The various stages are easily carried through.

New, systematic names are proposed for the alkaloids, the principal novelty being the adoption of Pasteur's nomenclature for the "toxines"; thus, "quinotoxine" becomes "quinicine." The new names are given in brackets.

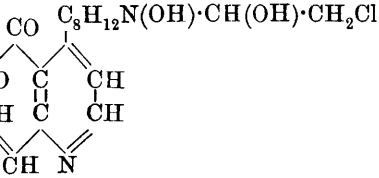
Dihydrocinchonine (cinchotine) hydrochloride is boiled with sodium acetate and 50% acetic acid for several hours, the product is rendered alkaline, and the cinchotoxine (cinchoticine) is extracted with ether and converted into *benzoylcinchoticine* (annexed formula), which crystallises in groups of white needles, m. p. 124°. This forms an oily *dimethosulphate*, the *picrate* of which has m. p. 152—154°. When the benzoylcinchoticine is boiled with chromic acid in glacial acetic acid solution and the product is diluted and extracted with ether, cinchonic acid is found in the aqueous portion and benzoylcincholeupone, with much unchanged material, in the extract. The two acids are isolated first as their copper salts. The dimethosulphate undergoes a different fission on oxidation with permanganate. The quinoline nucleus is removed as formylmethylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NMe\cdot COH$, whilst the piperidine nucleus is apparently preserved in benzoylhomocincholeupone (1-benzoyl-5-ethylpiperidine-4-propionic acid). This could not be purified, but was transformed by hydrolysis and esterification into ethyl 5-ethylpiperidine-4-propionate, b. p. 136°/11 mm.



The iso*nitrosobenzoylcinchoticine* is readily obtained by the action of amyl nitrite in the presence of sodium ethoxide in white needles, m. p. 175—177°, and is quantitatively transformed into cinchonic acid and *benzoylcincholeupononitrile* (1-*benzoyl*-5-*ethylpiperidine*-4-*acetonitrile*), b. p. 160—165°/mercury vacuum, when a solution in 5% sodium hydroxide is shaken with *p*-toluenesulphonyl chloride at 45°. The nitrile is conveniently hydrolysed to cincholeupone (5-ethylpiperidineacetic acid) and benzoic acid by warming with 70% sulphuric acid. J. C. W.

Thalleioquinine. A. Christensen (*Ber. Deut. pharm. Ges.*, 1916, **26**, 249—261. Compare A., 1915, i, 711).—In extension of his investigation on the action of chlorine on quinine, the author has turned his attention to the nature of the green substance, thalleioquinine, of which a solution is obtained when a quinine salt is treated successively with solutions of chlorine and ammonia. The thalleioquinine prepared by the action of aqueous ammonia on the nitrate of the so-called 5-dichloro-6-ketocinchonine hydroxychloride (*loc. cit.*) was not pure, but appeared to contain some of the unaltered nitrate. Better results were obtained with the more soluble nitrate of the base derived from chlorohydroquinine (*loc. cit.*), which on careful treatment with aqueous ammonia gave a thalleioquinine of the composition $C_{19}H_{21}O_3N_2Cl,NH_3$; the molecule of ammonia is removable by keeping over phosphoric oxide in a vacuum, and the remaining substance probably has the structure of chloro-5 : 6-diketohydrocinchonine. The structure of the

thalleioquinine derived from quinine by the well-known chlorine–ammonia test is therefore probably that of chloro-5 : 6-diketo-hydroxycinchonine (annexed formula), also with the addition of a loosely bound molecule of ammonia. Evidence is adduced as to the ease with which a chlorine atom in the 5-position adjacent to a hydroxyl group in the 6-position of the quinoline nucleus of such compounds as the above is eliminated by the action of ammonia, the concurrent action of an oxidising substance causing the formation of a ·CO·CO· group. On this account, it is possible to prepare thalleioquinine analogues from 5-chloro-6-hydroxycinchonine hydrochloride by the action of silver sulphate or nitrate in the presence of potassium persulphate or lead dioxide in a dilute acid medium, with the subsequent addition of aqueous ammonia. In these reactions, the silver salt serves to effect the removal of the chlorine.



In an analogous manner, 5-chloro-6-hydroxyquinoline has been shown to be oxidisable to a compound which gives a green coloration with aqueous ammonia (Mathëus, A., 1888, 965), and it is now demonstrated that the oxidation may be effected with various other oxidising agents, such as lead dioxide, chlorine water, or a mixture of silver sulphate and potassium persulphate, in each case in the presence of dilute sulphuric acid. D. F. T.

Degradation of Scopoline. K. Hess (*Ber.*, 1916, **49**, 2337—2339. Compare A., 1916, i, 285).—A claim for priority against E. Schmidt (*ibid.*). J. C. W.

Fractionation of the Phosphotungstic Acid Precipitate with Acetone for the Preparation of Vitamine from Yeast. Casimir Funk (*Biochem. Bull.*, 1916, **5**, 1—16; from *Physiol. Abstr.*, 1916, **1**, 42).—The phosphotungstates from an alcoholic yeast extract are largely soluble in acetone; the bulk of the vitamine is, however, contained in a small fraction insoluble in acetone. Phosphotungstates may be decomposed with lead acetate, instead of barium hydroxide; this new method yields clear solutions, facilitates purification, and avoids the use of alkali. G. B.

The Condensation of Pyrrole-2-aldehyde with Ketones. Eva Lubrzynska (T., 1916, **109**, 1118—1120).—Although it has been suggested (Angeli and Marchetti, A., 1909, i, 12; Alessandri, A., 1915, i, 452, 988) that pyrrole-2-aldehyde exists in the hydroxymethylene form, the fact that the substance yields the usual condensation products of an aldehyde with *p*-nitrophenylhydrazine, hydroxylamine, and semicarbazide (Bamberger and Djerdjian, A., 1900, i, 309; Tschelincev and Terentjev, A., 1915, i, 452) proves that it can react in the aldehydic form. As an extension of the present knowledge of the reactions of the substance, the author has

effected the condensation of pyrrole-2-aldehyde in the presence of alkali with methyl ethyl ketone, yielding a pale yellow *substance*, $C_9H_{11}ON$; with acetophenone giving a yellow *substance*, $C_{13}H_{11}ON$, and with acetone producing a yellow *substance*, C_8H_9ON; the general structure of these products is probably represented by the formula $C_4H_4N\cdot CH\dot{:}CH\cdot COR$, or the tautomeric

$$\cdot C_4H_3N\dot{:}CH\cdot CH_2\cdot COR.$$

In the case of acetone a very small quantity of an intense orange-coloured *substance* was also obtained, possibly of the structure $CO(CH\dot{:}CH\cdot C_4H_4N)_2$. For experimental details see original.

D. F. T.

Preparation of Mononitrocarbazoles. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294016; from *J. Soc. Chem. Ind.*, 1916, **35**, 1149).—Carbazole or an *N*-alkyl, *N*-aryl, or halogen derivative is dissolved or suspended in an inert medium immiscible with water and treated with nitric acid. H. W.

Condensation of Thiobarbituric Acid with Aromatic Aldehydes. ARTHUR W. DOX and G. P. PLAISANCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2164—2166. Compare this vol., ii, 53).—The authors have condensed thiobarbituric acid in solution in 12% hydrochloric acid with a number of aromatic aldehydes in similar solution at the ordinary temperature. The following compounds are described:—

Benzylidenemalonylthiocarbamide, a lemon-yellow precipitate, readily soluble in pyridine and alkali hydroxides.

o-*Hydroxybenzylidenemalonylthiocarbamide*, a bright vermilion precipitate, giving with dilute ammonia or alkali hydroxides a deep wine-red colour, which rapidly disappears.

o-*Nitrobenzylidenemalonylthiocarbamide*, a greenish-yellow product.

p-*Methoxybenzylidenemalonylthiocarbamide*, a deep yellow precipitate.

4-*Hydroxy*-3-*methoxybenzylidenemalonylthiocarbamide*, brilliant, orange-coloured precipitate, giving with alkali hydroxides a mahogany-red solution, the colour of which rapidly disappears.

3 : 4-*Methylenedioxybenzylidenemalonylthiocarbamide*, a bright orange-coloured precipitate.

3 : 4-*Dihydroxyphthalylidenedimalonylthiocarbamide*, a reddish-brown precipitate, soluble in alkali hydroxides to a mahogany-red solution.

Cinnamylidenemalonylthiocarbamide, a bright orange-red precipitate.

None of these compounds could be melted without decomposition, the decomposition temperatures not being sharp. The condensation products from the three aldehydes having a hydroxyl group in the benzene nucleus all gave a deep red coloration with alkali hydroxides, the others remaining colourless. All the condensation products were soluble in these alkalis. The reaction was in every case practically quantitative.

Three aliphatic aldehydes were tried—formaldehyde, acetaldehyde, and citral—but failed to react under the above conditions.

W. G.

Preparation of Amino-derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Substitution Products. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294159, addition to D.R.-P., 287804; from *J. Soc. Chem. Ind.*, 1916, **35**, 1180).—Amino-derivatives of 2-phenylquinoline-4-carboxylic acid or its substitution products are prepared by condensing mono-acyl derivatives of phenylenediamines, their homologues, or substitution products with benzaldehyde, its homologues, or substitution products, and pyruvic acid, and saponifying the resulting *N*-acyl compounds (compare A., 1916, i, 333, 334).

H. W.

The 2-Thio-3-aryl-5 : 5-dimethylhydantoins. J. R. BAILEY and A. T. MCPHERSON (*J. Amer. Chem. Soc.*, 1916, **38**, 2523—2527).—The authors have repeated Stelzner's work on the preparation of 2-thio-3-*o*-tolyl-5 : 5-dimethylhydantoin (compare A., 1892, 149) and certain of its derivatives, and, as in the case of other similarly constituted thiohydantoins (compare Bailey and Randolph, A., 1908, i, 741, 742), have obtained compounds differing considerably in their m. p. from the figures given by Stelzner. The authors find that 2-thio-3-*o*-tolyl-5 : 5-dimethylhydantoin has m. p. 195·5°, and when desulphurised gives 3-o-*tolyl*-5 : 5-*dimethylhydantoin*, thin, prismatic plates, m. p. 172°. The thiohydantoin gives a *methyl* ether, m. p. 75°, which forms a *picrate*, m. p. 152°, a *platinichloride*, m. p. 220°, and a *sulphate*, m. p. 196°. *o*-Tolylthiourethane (compare Liebermann and Natanson, A., 1881, 45) was also obtained in a crystalline state, m. p. 37°.

W. G.

Organic Periodides. II. Periodides of Antipyrine, Iodoantipyrine, and Pyramidone. W. O. EMERY and S. PALKIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2166—2181. Compare Kippenberger, A., 1897, ii, 292, and Scholtz, A., 1899, ii, 390, 584; 1900, ii, 638).—The authors have succeeded in isolating periodides of antipyrine, iodoantipyrine, and pyramidone in a crystalline form. Preliminary examination of the behaviour of antipyrine towards a solution of iodine in potassium iodide gave results confirming those of Scholtz (*loc. cit.*), as opposed to those of Kippenberger (*loc. cit.*). When a solution of iodine in aqueous potassium iodide is added to an acidified aqueous solution of antipyrine a tarry product is obtained in every case. The amount of iodine removed from solutions varies inversely with the amount of mineral acid present and directly with the amount of iodine added for a given weight of antipyrine. The limit of iodine removable is approximately four atoms for each molecule of antipyrine. A certain amount of the iodine is substituted in the molecule, the amount varying with the concentration of the iodine and the mineral acid.

From the tars precipitated under the above conditions it is possible by use of suitable solvents to isolate crystalline periodides,

but these are best prepared by the admixture of antipyrine, hydriodic acid, and iodine in organic solvents, the most satisfactory being alcohol, ether, or ethyl acetate. By varying the quantities of the three substances used the following compounds were obtained.

Triantipyrine dihydriodotetriodide, $(C_{11}H_{12}ON_2)_3,(HI,I_2)_2$, steely-blue, needle-like prisms, D 1·91, m. p. 79—80°, having a metallic lustre. They were odourless when dry and quite stable in the air.

Diantipyrine hydriododi-iodide, $(C_{11}H_{12}ON_2)_2,HI,I_2$, slender, glistening, ruby-red needles, m. p. 96—97°.

Iodoantipyrine was readily prepared by adding a $N/10$-solution of iodine in potassium iodide to a solution of 2 grams of antipyrine and 1 gram of sodium hydrogen carbonate in water at 50° until a faint yellow colour persisted after stirring. On cooling, colourless needles of iodoantipyrine separated, and from it, by the above methods, the following periodides were prepared:

Di-iodoantipyrine hydriododi-iodide, $(C_{11}H_{11}ON_2I)_2,HI,I_2$, ruby-red needles, m. p. 124—125°.

Di-iodoantipyrine hydriodotetriodide, $(C_{11}H_{11}ON_2I)_2,HI,I_4$, chocolate-coloured prisms, difficult to purify.

Di-iodoantipyrine hydriodohexiodide, $(C_{11}H_{11}ON_2I)_2,HI,I_6$, dark green, glistening, acicular prisms, m. p. 97—98°.

Two crystalline periodides were prepared from pyramidone hydriodide in a similar manner. Pyramidone hydriododi-iodide, $C_{13}H_{17}ON_3,HI,I_2$, ruby-red needles, m. p. 190° (compare Cousin, A., 1909, i, 190). *Pyramidone hydriodotri-iodide*, $C_{13}H_{17}ON_3,HI,I_3$, green, glistening leaflets, m. p. 155—156°.

Both these periodides can be prepared directly from pyramidone itself by dissolving the components in alcohol and allowing the resulting additive product to separate slowly by crystallisation.

W. G.

The *cyclo*Pentadiene Series. IV. The Formation of *cyclo*Pentadienedihydropyridazines. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1916, **38**, 2535—2545).—The monohydrazones and phenylhydrazones of 5-nitro-2:3-diacetyl*cyclo*pentadiene and the corresponding dibenzoyl compound have been shown to be unstable (compare A., 1912, i, 994; 1913, i, 184, 369), undergoing intramolecular condensation with the production of coloured compounds. These have now been studied, and their products of oxidation determined.

When 5-nitro-2:3-diacetyl*cyclo*pentadiene in solution in aqueous sodium carbonate is treated with hydrazine sulphate, a yellow precipitate of the hydrazone is formed at first, and then redissolves, and finally an orange-red precipitate of 6-*nitro*-1:4-*dimethyl*-cyclo*pentadienedihydropyridazine*, $NO_2{\cdot}C{<}\begin{matrix}CH{\cdot}C{:}CMe{\cdot}NH\\ CH{:}C{\cdot}CMe{:}N\end{matrix}$, red prisms, m. p. 240—245° (decomp.), is obtained. When this substance is dissolved in just sufficient aqueous potassium hydroxide to form the potassium salt and oxidised with 4% potassium permanganate on a water-bath, it yields 3:6-*dimethylpyridazine*-4:5-*di*-

carboxylic acid, $C_4N_2Me_2(CO_2H)_2$, colourless prisms, m. p. 226—228° (decomp.). It gives a white, insoluble *silver* salt.

If an excess of phenylhydrazine is added to an alcoholic solution of 5-nitro-2 : 3-diacetyl*cyclo*pentadiene and the mixture warmed for an hour, *6-nitro-2-phenyl-1 : 4-dimethyl*cyclo*pentadiene-dihydropyridazine*, $NO_2\cdot C{<}\begin{matrix}CH\cdot C{:}CMe\cdot NPh \\ CH{:}C\cdot CMe{:}N\end{matrix}$, yellow needles, m. p. 193°, is obtained. This compound, when oxidised in acetone solution with potassium permanganate in the same solvent, yields *4-keto-1-phenyl-3 : 6-dimethyl-1 : 4-dihydropyridazine-5-carboxylic acid*, colourless needles, m. p. 220°, and oxalic acid.

When 5-nitro-2 : 3-dibenzoyl*cyclo*pentadiene in benzene–alcohol solution is warmed with an excess of hydrazine hydrate in alcoholic solution for a few hours, *6-nitro-1 : 4-diphenyl*cyclo*pentadiene-dihydropyridazine*, orange-red prisms, m. p. 275—280° (decomp.), is obtained. The original dibenzoyl compound, when digested in hot benzene solution with an excess of phenylhydrazine for eight hours, yields *6-nitro-1 : 2 : 4-triphenyl*cyclo*pentadienedihydropyridazine*, orange-red prisms, m. p. 287°. These two compounds were not submitted to the oxidising action of potassium permanganate.

W. G.

Manufacture of Anthracene Dyestuffs [Alkylated Pyrazole anthrone Yellow]. CHEMISCHE FABRIK. GRIESHEIM ELEKTRON (Brit. Pat., 14103; from *J. Soc. Chem. Ind.*, 1916, **35**, 1104).—Pyrazoleanthrone-yellow (A., 1913, i, 533) or an alkali salt is treated with an alkylating or arylating agent. Thus, pyrazoleanthrone-yellow (1 part) in the form of a paste is digested with 5% potassium hydroxide solution until completely converted into the violet potassium salt, the solution diluted until it contains 3—5% potassium hydroxide, and the salt drained as far as possible; the paste obtained is heated with benzyl chloride (1 or 2 parts) in a closed vessel at 100° for three hours, and the product is diluted with alcohol, filtered, and the residue washed with alcohol. The *monobenzyl* derivative produced gives with hyposulphite a blue vat, from which cotton is dyed scarlet shades. When the benzyl derivative (38 parts) in the form of the dried potassium salt is heated, with stirring, in an autoclave for one hour at 120° with methyl toluene-*p*-sulphonate (120 parts), the *benzylmethyl* derivative is obtained; this product dyes cotton an excellent fast red.

H. W.

Autoxidation of Benzaldehydephenylhydrazone in Alcohol. M. BUSCH and HERM. KUNDER (*Ber.*, 1916, **49**, 2345—2358. Compare A., 1915, i, 307).—Under the influence of air and light, alcoholic solutions of benzaldehydephenylhydrazone become red, owing to oxidation. Stobbe and Nowak (A., 1913, i, 1200) isolated from such a solution diphenyldibenzylidenehydrotetrazone, benzaldehyde, and benzoic acid, but it is now shown that the reaction is a very complicated one, and the existence of

the eight or nine products which the authors have obtained can be referred back very largely to the participation of the primary peroxide.

A suspension of benzaldehydephenylhydrazone (40 grams) in alcohol (600 c.c.) and glacial acetic acid (5 c.c.) is shaken with oxygen for about a day until no more gas is absorbed and solution is complete. A trace of diphenyldibenzylidenehydrotetrazone, $N_2Ph_2(N \cdot N:CHPh)_2$, usually separates towards the end in iridescent needles; these are removed, and the filtrate left to evaporate. In a day or two yellow needles (*A*) are deposited, followed by stout prisms (*B*) during the next few days. The mother liquor then becomes oily, and after about a week deposits a yellow powder (*C*), and contains much benzaldehyde and benzoic acid. After removing the acid by means of sodium carbonate solution, the dark mass which remains can be made to yield a further solid (*D*). The effect of temperature and of other acids (for example, tartaric) on the nature of the products is briefly mentioned.

The substance *A* is pure *benzoyldiphenylbenzylidenehydrotetrazone*, NHBz·NPh·NPh·N:CHPh, and crystallises in yellow needles, m. p. 105—106°. It may be reduced by means of zinc dust and acetic acid to benzaldehydephenylhydrazone and β-benzoylphenylhydrazine, and it is easily prepared by the condensation of benzaldehydephenylhydrazone with benzoylazobenzene. Inasmuch as the peroxide of benzaldehydephenylhydrazone suffers transformation into benzoylphenylhydrazine and benzoylazobenzene, the production of substance *A* can easily be accounted for. The yield of it is also considerably enhanced if β-benzoylphenylhydrazine is added to the alcoholic suspension at the outset.

Solutions of *A* in alcohol or benzene become dark red on boiling, especially in the presence of ammonia, owing to the production of *benzoylformazylbenzene*, NPhBz·N:CPh·N:NPh, which crystallises in brilliant, very dark red prisms, m. p. 139°, and sometimes in orange-red prisms, m. p. 146—147°. The two hydrogen atoms which are lost apparently go to the production of oily by-products. The compound may be reduced to a hydrazo-compound by mild agents, but zinc dust and sulphuric acid, on warming, give rise to the formation of α- and β-benzoylphenylhydrazines. Alcoholic hydrogen chloride causes a vigorous evolution of nitrogen and forms ethyl benzoate and α-benzoylphenylhydrazine hydrochloride.

Substance *B* is an isomeride of *A*, namely, *benzoylphenylhydrazinobenzaldehydephenylhydrazone*,

NHBz·NPh·CPh:N·NHPh,

and is obtained when the latter is left in a mixture of alcohol and acetic acid for about a week. It crystallises in almost colourless needles or columns, m. p. 177°, but combines readily with alcohol (stout leaflets) or benzene (white needles). It forms a *nitroso*-compound, brilliant, colourless, stout crystals, m. p. 114°, and may

be hydrolysed by dilute sulphuric acid to phenylhydrazine and $\alpha\beta$-dibenzoylphenylhydrazine.

Compound *C* is *benzeneazodiphenylmethane*, $NPh:N\cdot CHPh_2$; it forms deep lemon-yellow leaflets or needles, m. p. 74—75°, and changes into substance *D*, which is benzophenonephenylhydrazone, when an ethereal solution is left in contact with a trace of hydrogen chloride.

Some other benzoyldiphenylbenzylidenehydrotetrazones have been prepared; by the condensation of benzaldehyde-*p*-bromophenylhydrazone with benzoylazobenzene, the *compound*,

$$NHBz\cdot NPh\cdot N(C_6H_4Br)\cdot N:CHPh,$$

is formed, in pale yellow needles, m. p. 97—98°; benzaldehydephenylhydrazone and benzoylazo-*p*-bromobenzene yield the *isomeride*, $NHBz\cdot N(C_6H_4Br)\cdot NPh\cdot N:CHPh$, m. p. 109—110°, whilst *benzoyldi*-p-*bromophenylbenzylidenehydrotetrazone* crystallises in canary-yellow leaflets, m. p. 120—121°, and changes into the *formazyl* compound, garnet-red leaflets, m. p. 151°, on warming with benzene or alcohol and a trace of ammonia. J. C. W.

Aminohydrazines. III. *o*-Aminophenyl-β-benzylhydrazine. HARTWIG FRANZEN and BERTHOLD VON FÜRST (*Annalen*, 1916, **412**, 14—35. Compare A., 1907, i, 321; 1914, i, 206).—The remarkable property of *o*- and *p*-aminophenylbenzylidenehydrazines (benzaldehyde-*o*- and -*p*-aminophenylhydrazones) of yielding the phenylenediamine, ammonia, and benzaldehyde by treatment with hot acids may be due to the amino-group, to the double linking, or to both. These alternatives have now been investigated. All attempts to prepare *p*-aminophenyl-β-benzylhydrazine were unsuccessful. Benzaldehyde-*o*-aminophenylhydrazone, however, which reacts with phenylthiocarbimide in boiling alcohol to form the *phenylthiocarbamide*, $CHPh:N\cdot NH\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh$, pale yellow needles, m. p. 218—220°, with benzoyl chloride in cold pyridine to form the *benzoyl* derivative, $CHPh:N\cdot NH\cdot C_6H_4\cdot NHBz$, colourless leaflets, m. p. 190—193°, and with boiling alcoholic hydrogen chloride to form 2-phenylbenziminazole quantitatively, is reduced in boiling alcoholic solution by 3% sodium amalgam, yielding o-*aminophenyl-β-benzylhydrazine*, $NH_2\cdot C_6H_4\cdot NH\cdot NH\cdot CH_2Ph$, which is obtained in needles, m. p. 62—63°, to a turbid, yellow liquid clarifying at 80°, or after repeated crystallisation in citron-yellow needles, m. p. 73° (sharp). The substance decomposes within a few hours, develops in alcoholic solution an intense Bordeaux-red coloration with a few drops of mineral acid, and forms a *hydrochloride*, $C_{13}H_{15}N_3,2HCl$, violet-red powder, m. p. 201—202° (from an alcoholic solution of which the yellow hydrazine is regenerated by ammonia at −10°), the *phenylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot N(CS\cdot NHPh)\cdot N(CH_2Ph)\cdot CS\cdot NHPh$, colourless needles, m. p. 178—179°, the *phenylcarbamide*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot N(CO\cdot NHPh)\cdot NH\cdot CH_2Ph,$$

colourless, crystalline powder, m. p. 198°, and a *dibenzoyl* derivative, $NHBz\cdot C_6H_4\cdot NBz\cdot NH\cdot CH_2Ph$, colourless, crystalline powder, m. p. 179—180°.

In connexion with the intensely coloured salts of benzaldehyde-*p*-aminophenylhydrazone, the suggestion has been made (*loc. cit.*) that the intensification of the colour may be due to a change in the constitution from the hydrazone to the azo-structure. This explanation becomes untenable in view of the colour of *o*-aminophenyl-β-benzylhydrazine and its hydrochloride, to which azo-structure cannot possibly be attributed. The colour intensity must be due in some way to the presence of the amino-group, because the known phenylbenzylhydrazines and their salts are colourless, but in what way cannot be determined at present; explanations involving quinonoid structure or Wieland's theory of dissociation are shown to be inadequate.

When an alcoholic solution of *o*-aminophenyl-β-benzylhydrazine is boiled with 2*N*-sulphuric or hydrochloric acid, 2-phenylbenziminazole, benzylamine, *o*-phenylenediamine, and ammonia are produced. The formation of these four substances is explained, as in the case of the three similarly obtained from benzaldehyde-*p*-aminophenylhydrazone (*loc. cit.*), by the assumption of the intermediate formation of chloroamines, and an attempt is made to account for the ordinary benzidine and semidine transformations by a similar assumption.

By heating at 120—130° in an atmosphere of hydrogen, *o*-aminophenyl-β-benzylhydrazine is converted into benzaldehyde-*o*-aminophenylhydrazone, benzylamine, and *o*-phenylenediamine. The formation of these is explained by assuming that one molecule of the hydrazine dissociates into $NH_2\cdot C_6H_4\cdot NH\cdot$ and $CH_2Ph\cdot NH\cdot$; these are reduced by a second molecule of the hydrazine, which is itself oxidised to the azo-compound, the latter then undergoing rearrangement into the *o*-aminophenylhydrazone. C. S.

Aminohydrazines. IV. *p*-Acetylaminophenylhydrazine and Benzylidene-*m*-aminophenylhydrazine. HARTWIG FRANZEN and BERTHOLD VON FÜRST (*Annalen*, 1916, **412**, 35—48). Compare preceding abstract).—It has been shown that certain aminohydrazines form coloured salts and are easily ruptured at the N·N linking by warming with acids, and that these properties are due to the influence of the amino-group. The present investigation has been undertaken to ascertain what will be the effect on these properties of changes in the amino-group.

The crystalline precipitate obtained when diazotised monoacetyl-*p*-phenylenediamine hydrochloride is reduced by stannous chloride according to Riedel's method (D.R.-P., 80843) is not *p*-acetylaminophenylhydrazine hydrochloride, as there stated, but the stannochloride. The hydrochloride is a colourless, indistinctly crystalline substance which is stable by itself and in the presence of cold concentrated hydrochloric acid; the *nitrate* is also a colourless, crystalline powder. The *dibenzoyl* derivative,

$$NHAc\cdot C_6H_4\cdot NBz\cdot NHBz,$$

colourless, crystalline powder, has m. p. 155—156°, and the following p-*acetylaminophenylhydrazones* have been prepared: from benzaldehyde, $C_{15}H_{15}ON_3$, pale yellow, crystalline powder, m. p.

195—196° (the alcoholic solution gives with cold dilute hydrochloric or sulphuric acid an almost colourless, flocculent precipitate, whereas benzaldehyde-*p*-aminophenylhydrazone under these conditions gives an intensely violet-red precipitate); from *p*-anisaldehyde, $C_{16}H_{17}O_2N_3$, finely crystalline, red powder, m. p. 170—175°; from pyruvic acid, $C_{11}H_{13}O_3N_3$, deep yellow, crystalline powder, m. p. 192—193°.

When heated with dilute hydrochloric acid, *p*-acetylaminophenylhydrazine hydrochloride remains colourless at first, but then the solution suddenly becomes intensely yellow and nitrogen is evolved; the other products of the decomposition are ammonia, aniline, *p*-phenylenediamine, and acetic acid. It appears, therefore, that the N·N linking is not ruptured until the acetylamino-group has been hydrolysed, and that the salts of *p*-aminophenylhydrazine, like those of the ortho-derivative and of benzaldehyde-*p*-aminophenylhydrazone, are intensely coloured.

Benzaldehyde-m-*aminophenylhydrazone*,

$$CHPh:N \cdot NH \cdot C_6H_4 \cdot NH_2,$$

brownish-yellow needles, m. p. 154—155°, is obtained, like the ortho- and para-isomerides (*loc. cit.*), by reducing the corresponding benzaldehyde-*m*-nitrophenylhydrazone with sodium hyposulphite, but the yield is extremely small (14%). The substance is stable, forms a *dibenzoyl* derivative, colourless leaflets, m. p. 210°, and a *phenylthiocarbamide*, $CHPh:N \cdot NH \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, faintly red, crystalline powder, m. p. 138—139°, and yields a *sulphate*, $2C_{13}H_{13}N_3,H_2SO_4$, colourless needles, m. p. 218°, and *hydrochloride*, colourless leaflets.

From these and the preceding results (*loc. cit.*) the conclusions are drawn: (1) a relation exists between the colour and the stability of the salts of aminophenylhydrazines; coloured salts are very easily ruptured at the N·N linking, whilst colourless salts are not; (2) the loosening effect of the amino-group on the N·N linking is much greater when the amino-group is in the ortho- or para-position than when it is in the meta-position, and is diminished when the amino-group is acetylated. C. S.

The Phosphorus contained in Animal Proteins after their Demineralisation. L. LINDET (*Bull. Soc. chim.*, 1916, [iv], **19**, 395—399. Compare A., 1912, i, 1041).—The protein precipitated from the white of egg by phenol in the presence of 2% acetic acid contains no organic phosphorus. When the vitellin is separated from the yolk of an egg by precipitation with toluene, ether, or 10% saline or 1% phenol, this material, after removal of the fat and washing with 2% acetic acid, contains organic phosphorus to the extent of 3·6—3·7% P_2O_5 on the protein precipitated. The protein of blood contains no organic phosphorus, neither does gelatin or ossein. Of the protein in the fibrin of an ox, the liver of a calf, or the brain of a sheep, the portion which is insoluble in saline solution contains organic phosphorus to the extent of 0·25—1·82% P_2O_5 on the total protein. The flesh of fish contains

no organic phosphorus, either in the portion soluble or insoluble in saline solution. W. G.

The Composition of Neurokeratin. BURT E. NELSON (*J. Amer. Chem. Soc.*, 1916, **38**, 2558—2561).—The neurokeratin was obtained from the total protein residue from several lots of brains of patients having general paresis, senile dementia, and dementia præcox. The minced brain tissues were allowed to remain in 85% alcohol for two months, and then extracted with alcohol, ether, and warm water. The dried protein residue was finely ground and digested at blood heat six times with one hundred times its weight of pepsin–salt–hydrochloric acid mixture and then five times with a 0·1% solution of sodium hydroxide, and finally extracted with alcohol and ether and dried at a gentle heat. The neurokeratin thus obtained was a pale yellow, light powder containing 0·22—0·25% mineral ash. Its elementary composition averaged C, 54·87%; H, 7·28%; N, 13·17%, S, 1·38%; O, 23·07%; ash, 0·23%. Phosphorus was entirely absent. A single partition of the nitrogen content, made by a modification of van Slyke's method, gave: ammonia N, 5·24%; melanin N, 14·51%; arginine N, 2·692%; cystine N, 4·40%; histidine N, 6·279%; lysine N, 11·729%; nitrogen from one or all of pyrroline, oxypyrroline, or tryptophan, 27·95%; nitrogen from one or all of glutamic acid, aspartic acid, tyrosine, leucine, *iso*leucine, alanine, or glycine, 25·21%. The results of this fractionation indicate that most of the sulphur exists in the form of cystine. W. G.

Formaldehyde as a Prototype of Diastase. Theory of the Action of Diastase. GERTRUD WOKER (*Ber.*, 1916, **49**, 2311—2318).—The author has already shown that formaldehyde can produce the effects of a peroxydase or a catalase, and has explained this by the assumption that the ferments are aldehydic in character and that they form additive compounds with hydrogen peroxide, to which their activities can be traced, thus: $H{\cdot}CHO + H_2O_2 = OH{\cdot}CH_2{\cdot}O{\cdot}OH$. It is now recognised that diastase can behave as a peroxydase or catalase, and the question arises: Can its more important hydrolytic functions be also due to an aldehyde group, or can its action on starch be imitated by formaldehyde? It is conceivable that formaldehyde might form a hydrate which, on decomposition, would offer the elements of water, H and OH, in an active form. Experiments show that solutions of starch and glycogen do, indeed, suffer hydrolysis when left in the presence of relatively large quantities of formaldehyde, although the aldehyde is more pronounced as a prototype of a peroxydase than of diastase. This throws some light on the fact that, although formaldehyde is a powerful poison for enzymes, a 2—5% solution of it actually accelerates the action of diastase. J. C. W.

The Influence of the Hydrion Concentration on the Activity of Malt Diastase. LUDWIG ADLER (*Biochem. Zeitsch.*, 1916, **77**, 146—167).—The optimal hydrion concentration for the

action of this diastase is $p_H = 4 \cdot 9$. Its action is very effective between the limits $p_H = 4 \cdot 6$ and $p_H = 5 \cdot 2$. As the hydrion concentration passes these limits in either direction, the activity of the ferment rapidly decreases. Neutral salts are not without action on the diastatic activity, but this influence is small compared with the hydrion concentration. S. B. S.

Studies in Fermentation. II. Autolysis of Starch. W. BIEDERMANN (*Chem. Zentr.*, 1916, ii, 496; from *Fermentforschung*, 1916, **1**, 474—504).—The author has previously shown that dilute boiled starch solution can be hydrolysed with comparative rapidity by saliva ash, and that this effect is due to a ferment liberated from the starch under the conditions of experiment. It is now shown that a similar hydrolysis (autolysis) occurs without any addition if the starch solution is made at 70—90°. Reaction occurs considerably more rapidly at 35—45° than at the ordinary temperature, and only the portion of starch which remains in solution suffers autolysis. Solutions which have been actually boiled generally become hydrolysed after a much longer period; extracts prepared by grinding starch with water do so much more rapidly. The diastatic power of the latter is similar to that of a very dilute saliva solution, and transforms starch completely into sugar. Of the salts contained in saliva, the chlorides, particularly calcium chloride, promote diastatic action. The marked action of saliva ash in promoting the decomposition of starch solutions which have been subjected to prolonged boiling suggests that this mixture of salts promotes the new formation of the diastase (amylose) from starch. The action of the ash is much more pronounced than that of the individual chlorides ($CaCl_2$, NaCl, KCl) contained in it; artificial mixtures of salts of similar activity have not been prepared up to the present time. H. W.

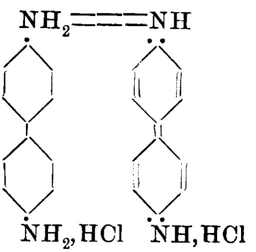
Relation of Oxydase Reactions to Changes in Hydrogen Ion Concentration. GUILFORD B. REED (*J. Biol. Chem.*, 1916, **27**, 299—302).—In these experiments, extracts of potato or apple containing oxydase are incubated with increasing quantities of acid, the concentration of hydrogen ion in the incubating mixture being estimated by the gas-chain method. The results indicate that the optimal activity of these oxydases is reached when they are in a medium which is very nearly neutral or slightly alkaline. The concentrations of acid which are needed to inhibit oxydase action are found to be much lower than those stated by previous investigators, who have measured the acid added to the oxydase solution, but not the resultant acidity of the medium. As a matter of fact, it is found that a large proportion of the added acid is neutralised by the protein and other amphoteric substances present in the solution. H. W. B.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. GERTRUD WOKER (*Ber.*, 1916, **49**, 2319—2337).—Kjöllerfeldt, a colleague of the author, has ex-

perienced considerable difficulty in the application of benzidine hydrochloride to the determination of peroxydase activities, particularly in the preparation of a reagent of constant and maximum pigment-forming power. He finds that the most active reagent can be obtained by adding enough alkali to the dihydrochloride to neutralise one molecule of the acid, or by adding this quantity of acid to the free base. This salt crystallises in leaflets, is almost insoluble in cold water, and begins to decompose at about 160°, its m. p. being 341°. Other preparations which are more soluble and more stable towards heat have not the same activity. One, of the same acid content (B,HCl), can be obtained under some conditions, which crystallises in rods, melts without decomposition at 341—342°, has the solubility 70% at 20°, and gives no blue colour under the influence of a peroxydase.

It is furthermore recognised that many of the so-called "activations" and "paralysations" of peroxydases which have been apparently effected by the addition of acids or bases are due to the action of these agents on the test solution, benzidine, and probably not on the ferment at all. The right conditions for the best production of benzidine-blue are realised when the solution contains little or no free hydrochloric acid. The readily soluble hydrochlorides suffer extensive hydrolysis, and their solutions are consequently less active, whilst the insoluble salts are the most active reagents. On keeping, or on washing with water, benzidine dihydrochloride becomes more and more active, owing to the loss of hydrochloric acid.

The oxidation of benzidine is a very complicated question, and the work on the subject is well reviewed. The blue, *meri*-quinonoid oxidation product, which is the one concerned in the peroxydase reaction, is regarded as a compound of benzenoid benzidine with a quinone–imine molecule and two molecules of hydrogen chloride. Instead of assuming that these molecules are attached by partial valencies, the author prefers the annexed arrangement. This helps to explain the special activity of one benzidine monohydrochloride and the inactivity of another. When the dihydrochloride is deprived of a molecule of hydrogen chloride, it is assumed that two molecules of the salt participate, giving the *cis*- and *trans*-"dibenzidine" salts,



$NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2,HCl$
$NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2,HCl$ and

$HCl,NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$
$NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2,HCl.$

The *cis*-form is the readily oxidisable one and has the ring systems of the *meri*-quinonoid dye already in it. It may undergo

isomerisation into the inactive *trans*-form under the influence of acids, or acids may break up the double molecule, with the result, in either case, that the salt will be inactive. J. C. W.

Physiological Chemistry.

The "Reduced" and "Regulated" Hydrogen Number of the Blood. OTTO PORGES (*Biochem. Zeitsch.*, 1916, **77**, 241—248).—This paper contains a criticism of Hasselbalch's conceptions (A., 1916, i, 519) of the "reduced" (that is, under 40 mm. tension of carbon dioxide) and "regulated" (under the tension of the carbon dioxide of alveolar air) hydrion concentration of the blood. It is based partly on what the author considers a faulty method for the estimation of the tension of carbon dioxide in alveolar air employed by Hasselbalch and his collaborators. The author also objects to Hasselbalch's suggestions as to the employment of the term "acidosis." S. B. S.

The Blood of Participators of an Army March with Accoutrements. II. Residual Nitrogen and its Components, Blood-sugar and Density. JOH. FEIGL (with A. V. KNACK and H. KOOPMANN) (*Biochem. Zeitsch.*, 1916, **76**, 297—312. Compare A., 1916, i, 769).—The chief results refer to the residual nitrogen of the blood. In most cases the effect of vigorous exercise is to increase the amount of urea in the blood. S. B. S.

The Total and Residual Reduction by the Blood with Special Reference to the Reducing Components of the Residual Nitrogen; the Estimation of Blood-sugar under Normal and Pathological Conditions. JOH. FEIGL (*Biochem. Zeitsch.*, 1916, **77**, 189—231).—A general summary is given, with copious references to the literature, of the work done on estimation of the non-protein nitrogenous constituents of serum and their capacity for reducing reagents employed for estimating sugars. Attempts are made to estimate approximately the deductions to be made in the estimation of sugars due to the presence of such nitrogenous substances in normal and pathological cases ("residual reduction"). Attention is also directed to the influence that can be exerted by the various methods employed for the precipitation of proteins. S. B. S.

Colourless Crystals of Hæmoglobin. D. FRASER HARRIS (*Nature*, 1916, **96**, 619; from *Physiol. Abstr.*, 1916, **1**, 53).—A note on colourless crystals arising in laked blood and on crystals

originally indistinguishable from hæmoglobin which have become decolorised. Boycott (*ibid.*, 677) suggests that the crystals are serum protein, some of which are tinged with hæmoglobin.

G. B.

Growth. VIII. Influence of a Diet Deficient in Fats, and of the same Diet with Cholesterol added, on the Growth of the White Mouse. T. Brailsford Robertson (*J. Biol. Chem.*, 1916, **27**, 393—402. Compare A., 1916, i, 690).—A diet composed of potatoes, defatted bran, and white of egg, with the addition of small amounts of chlorophyll and ferric chloride, when fed to young mice leads to initial loss of weight followed by resumption of a retarded growth. Ultimately, however, a sharp decline in weight occurs, which terminates in death about six months after the beginning of the experiment. The addition of cholesterol to the diet prevents the initial loss of weight, but does not prolong the life of the mouse. The author suggests that although growth is possible on the described diet, the tissue produced is unable to be maintained. H. W. B.

Mechanism of Cholesterol Absorption. J. Howard Mueller (*J. Biol. Chem.*, 1916, **27**, 463—480. Compare A., 1915, i, 1026).—Experiments in vitro indicate that free cholesterol, in the presence of fatty acids and a suspension of pancreas, undergoes esterification, presumably by the operation of the pancreatic lipase. The action appears to be accelerated by the bile. Ordinary lipases do not saponify cholesterol esters, neither has the reverse action been observed except in the case of the pancreatic lipase already mentioned.

An examination of the intestinal mucosa of the dog reveals the presence of a large amount of esterified cholesterol after feeding. The author suggests that esterification occurs in the lumen of the intestine under the influence of the pancreatic juice, and the esters are absorbed as rapidly as they are formed. H. W. B.

Nutrition and Evolution. II. Jacques Loeb and J. H. Northrop (*J. Biol. Chem.*, 1916, **27**, 309—312. Compare A., 1916, i, 189).—Further experiments with banana flies have shown that successive generations of these insects can be reared on sterile food provided it contains yeast, which appears to be an indispensable food for them. The yeast may be previously heated for an hour at 120°, but cannot be replaced by its alcoholic extract or by butter, milk, nucleic acid, or other material. The necessary substance cannot therefore be identical with the accessory substances indispensable for the growth of pigeons, rats, and other warm-blooded animals.

The results indicate that animals as high in the scale of life as insects could not have existed without the previous existence of yeast. H. W. B.

Calcium Metabolism. I. Deposition of Lime Salts in the Integument of Decapod Crustacea. J. H. Paul and J. S. Sharpe (*Journ. Physiol.*, 1916, **50**, 183—192; from *Physiol. Abstr.*, 1916, **1**, 61—62).—After moulting, calcium carbonate is rapidly deposited in the shell of decapod crustaceans. In the edible crab, 80% of the shell is calcium carbonate, but in the lobster, calcium phosphate forms a large bulk of the inorganic matter. In the crab, calcium phosphate is present in the hepato-pancreas to the extent of 20% of the bulk of the gland immediately before moulting; after the shell has hardened, this salt is nearly absent from the gland. The lobster, on the other hand, does not store calcium in its hepato-pancreas, and the stone crab (*Lithodes maia*) does so only to a slight extent. Before moulting, the hepato-pancreas contains 20—50% of oil, which disappears, like the calcium, when the shell hardens. Its iodine value is in inverse order to the quantity of oil and to the quantity of calcium. After moulting, the blood-volume increases tenfold, but its percentage of calcium remains constant. It is present as salts of fatty acids, particularly formic and butyric. G. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. I. The Necessity of a General Salt Effect on the Membrane as a Prerequisite for this Diffusion. Jacques Loeb (*J. Biol. Chem.*, 1916, **27**, 339—352).—Experiments on *Fundulus* eggs are described, the results of which indicate that the diffusion of potassium chloride through the membrane of the egg does not depend only on the osmotic pressure of the potassium chloride solution, but on the production of a certain modification of the membrane, which is termed the "general salt effect." This modification is produced by the action of salts on the external surface or layer of the membrane (presumably on the proteins of the membrane). There is a concentration of the total salts in a solution which accelerates to the greatest extent the diffusion of one of these, for example, potassium chloride through the membrane. When the concentration is increased beyond this optimum, the rate of diffusion is diminished, and eventually the opposite action is observed, namely, the retardation or prevention of the diffusion of the potassium salt. This constitutes the "antagonistic salt action." H. W. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. II. Diffusion of Potassium Chloride out of the Egg of Fundulus and the Relative Efficiency of Different Ions for the Salt Effect. Jacques Loeb (*J. Biol. Chem.*, 1916, **27**, 353—362. Compare preceding abstract).—The author finds that eggs previously poisoned with potassium chloride do not recover when put into a solution of any non-electrolyte. When the external surface of the membrane, therefore, is free from salts, it is as efficient a barrier for the diffusion of potassium chloride out of the egg as for diffusion in the opposite direction.

The relative efficiency of different salts for producing the salt effect on the cell-membrane is a function both of anion and cation. The efficiency increases with the valency of the anion approximately according to Hardy's rule, and depends also on the nature of the anion in the following way: chloride, nitrate$<$bromide$<$acetate$<$ phosphate, carbonate$<$sulphate$<$citrate. With regard to the cation, the salts of sodium, lithium, magnesium, calcium, and ammonium favour the diffusion of potassium chloride through the membrane, whilst barium, strontium, rubidium, and cæsium inhibit it. H. W. B.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. III. Analogy of the Mechanism of the Diffusion for Acids and Potassium Salts. Jacques Loeb (*J. Biol. Chem.*, 1916, **27**, 363—375. Compare preceding abstracts).—Under certain experimental conditions, the author finds that similar rules hold for the diffusion of acids through the membranes of living eggs of *Fundulus* as for the diffusion of potassium salts. The concentration of neutral salt required for the production of the salt effect is considerably smaller in the case of the diffusion of acid than in that of potassium salt. Very weak acids themselves can supply the general salt effect, owing probably to the fact that acids form stable salts with certain proteins of the membrane, whilst neutral salts form only unstable salts.

When the concentration of neutral salt added to the acid is a little higher than that required for the production of the salt effect, the opposite phenomenon is produced, namely, the diffusion of acid is retarded or arrested (antagonistic salt action). H. W. B.

The Oxidation of Alcohol by the Liver of Animals which have acquired Tolerance and of those which have not. Julius Hirsch (*Biochem. Zeitsch.*, 1916, **77**, 129—145).—In the presence of oxygen and at 37° alcohol is destroyed by the livers of animals which have not acquired tolerance. The capacity for destroying alcohol is either inhibited or annihilated by heating the liver or in the presence of ferment poisons, such as cyanides. The destruction of alcohol is apparently due to a ferment. The pressed juice of the liver dried at the ordinary temperature is also active. The liver paste of animals (rabbits) which have acquired tolerance to alcohol is also active, but not more so than that of normal animals. S. B. S.

Phosphatides in the Ductless Glands. Frederic Fenger (*J. Biol. Chem.*, 1916, **27**, 303—307).—Light petroleum extracts relatively larger quantities of phosphatides and fats from the pituitary, suprarenal, pineal, and thymus glands and the corpus luteum than from ordinary muscle tissue. The thyroid gland, on the other hand, contains about the same proportion of these substances as muscle. The author draws the conclusion that phosphatides are

concerned in the operation of most ductless glands, but not in the elaboration of the secretion of the thyroid. H. W. B.

Vital Oxidation of Succinic Acid. The Chemical Kinetics of a Physiological Process. A. WESTERLUND (*Lunds. Univ. Årsskrift*, 1916, **12**, [N.F.], reprint, 19 pp.; from *Physiol. Abstr.*, 1916, **1**, 133).—The absorption of oxygen by an aqueous solution of succinic acid containing suspended minced horse muscle follows the course of a bimolecular reaction. With excess of the agent, the reaction velocity was computed, by means of the method of least squares, for air mixtures with different percentages of oxygen. The reaction velocity is increased with increasing percentage of oxygen, but only up to a limit, representing the oxygen content of atmospheric air. In a gas mixture with more oxygen the absorption is only accelerated to a very small degree. G. B.

Narcosis. V. RUDOLF HÖBER (*Biochem. Zeitsch.*, 1916, **77**, 51—52).—Some remarks on a recent paper by Winterstein (A., 1916, i, 616); the author claims priority to Lillie with regard to certain conceptions as to the action of narcotics on cell permeability. S. B. S.

Narcosis. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1916, **77**, 53—54).—A reply to the above remarks of Höber. S. B. S.

Influence of Parturition on the Composition and Properties of the Milk and Milk Fat of the Cow. C. H. ECKLES and LEROY S. PALMER (*J. Biol. Chem.*, 1916, **27**, 313—326). —Colostrum milk obtained after parturition contains relatively large quantities of protein and salts and small quantities of lactose and fat. Colostrum milk fat has a higher melting point and lower saponification and Reichert numbers than ordinary milk fat.

The length of time the cow is dry before parturition is a factor influencing the composition of colostrum milk. The shorter the time the cow is dry, the more closely does the colostrum milk resemble normal milk. When cows are milked up to the time of parturition, both the colostrum milk and milk-fat do not differ greatly from normal milk and milk-fat. The chief difference in these circumstances is an increase in the content of heat-coagulable protein in the milk. H. W. B.

The Connexion between the Metabolism of Phosphates and Carbohydrates in Diabetes. HANS EULER and OLOF SVANBERG (*Biochem. Zeitsch.*, 1916, **76**, 326—334).—The effect of the administration to diabetic patients of a preparation made by extraction of dried yeast and separation from the extract of the inorganic phosphates and proteins was investigated. This preparation should contain the co-enzyme. In some cases it caused a diminution of the excretion of sugar in the urine, which was accompanied by a diminution of total phosphates. S. B. S.

Pancreatic Diabetes in the Dog. I. Influence of Alkali and Acid on the Glycosuria and Hyperglycæmia. J. R. MURLIN and B. KRAMER (*J. Biol. Chem.*, 1916, **27**, 481—498).—The administration of sodium carbonate has the same inhibiting action on the glycosuria of pancreatic diabetes as is exerted in the case of other glycosuric conditions (compare Pavy and Godden, A., 1912, ii, 68). Hydrochloric acid has the reverse action and increases the glycosuria, whilst sodium and potassium hydrogen carbonates do not produce any marked effect. H. W. B.

Pancreatic Diabetes in the Dog. II. Is the Dextrose retained when Sodium Carbonate is administered to Depancreatised Dogs deposited as Glycogen? B. KRAMER, J. MARKER, and J. R. MURLIN (*J. Biol. Chem.*, 1916, **27**, 499—515. Compare A., 1916, i, 348, and preceding abstract).—A full account of work previously published. H. W. B.

Pancreatic Diabetes in the Dog. III. Influence of Alkali on the Respiratory Metabolism after Total and Partial Pancreatectomy. J. R. MURLIN and B. KRAMER, with J. A. RICHE (*J. Biol. Chem.*, 1916, **27**, 517—538. Compare preceding abstracts).—The administration of sodium carbonate to partially depancreatised dogs is followed by an increase in the respiratory metabolism, which is not observed in the case of fully depancreatised animals. H. W. B.

Maize Diet and its Connexion with Pellagra. P. SUÁREZ (*Biochem. Zeitsch.*, 1916, **77**, 17—26).—A method is described for the extraction of the fluorescing substance which is contained in maize. It is shown that this acts photodynamically on red blood corpuscles and on *Paramoecium coli*, and also on rabbits at the point of injection. On the other hand, the administration of "zeochin," as the fluorescing substance is called, when added to their diet, produces no photodynamic effect on mice. When, however, mice or pigeons have been fed on a diet composed exclusively of maize, they develop an illness similar to beri-beri, the symptoms of which rapidly disappear after administration of yeast. The assumption is made by the author that pellagra is due to a deficiency of some accessory food-stuff in the diet, and that on the same diet, in the condition produced by the deficiency, the "zeochin" exerts a photodynamic effect. S. B. S.

The Sensitising Action of the Natural Porphyrins. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1916, **77**, 268—272).—A crude porphyrin obtained from the urine of a patient with lead-poisoning was photodynamically active when tested with red blood corpuscles and paramœcia. The porphyrin of the worm *Eisenia foetida*, which in vivo acts as a protection against light, can act as a light sensitiser in vitro. Hence one and the same pigment can exist in a sensitising and non-sensitising form. Facts of this description show the possibility of porphyrinuria with and without light sensibility. S. B. S.

A New Group of Antagonising Atoms. I. T. P. FEENSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 99—104).—If a Ringer-Locke solution from which the potassium salt has been omitted is perfused through a frog's heart, the latter, as is well known, ceases to beat after a certain time in diastole. It has been found by the author that the addition of uranium nitrate in certain quantity to the potassium-free Ringer fluid can cause the heart to beat again normally. Too large an excess of uranium salt will, however, cause heart action to cease again, but this action can be antagonised by the addition of more calcium salt. In a Ringer solution, the ratio of $UO_2(NO_3)_2:CaCl_2$ appears to be about 1:24. S. B. S.

Fate of Alkali-Blue in the Organism. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1916, **27**, 377—391).—Alkali-blue injected intravenously into rats, rabbits, or dogs appears rapidly in the lymph in both leuco and free forms. The lymph flow is not markedly affected by the injection of the dye.

When administered parenterally, alkali-blue is eliminated chiefly in the bile. It appears to act as a cholagogue. It is not eliminated by the kidneys (except in traces), nor, after intravenous injection, by the alimentary tract. H. W. B.

Physiological and Pharmacological Studies on Coal-tar Colours. I. Fat-soluble Dyes. WILLIAM SALANT and ROBERT BENGIS (*J. Biol. Chem.*, 1916, **27**, 403—427).—Fat-soluble dyes, when given to rats, cats, or rabbits with the food or injected subcutaneously or intravenously, are eliminated in the urine and in the bile. In two particular cases it was found that the dyes were eliminated in the form of conjugated glycuronates. *Benzeneazoresorcinol glycuronate*, $C_{18}H_{20}O_9N_2$, crystallises in long, yellow prisms, m. p. 189—190° (decomp.). *Benzeneazophenol glycuronate*, $C_{18}H_{20}O_8N_2$, crystallises from dilute alcohol in yellow, rectangular plates or, sometimes, acicular prisms, m. p. 164—165° (decomp.). On hydrolysis, the corresponding dyes are obtained. It is probable that similar compounds were formed in the cases of the other dyes examined, although they were not isolated from the urine.

Histological examination showed that most of the dyes were deposited in the adipose tissue; staining of the nervous tissue, the kidney, and muscle was also observed in some experiments. The toxicity of the dyes was not pronounced even when large doses were administered. H. W. B.

The Pharmacology of Saponins. A. W. VAN DER HAAR. (*Biochem. Zeitsch.*, 1916, **76**, 350—358).—Some experiments showing differences in different preparations of saponin as regards toxicity to fish and frogs, and also as to hæmolytic action.

S. B. S.

The Action of Cobra Poison on Lecithin. R. KUDICKE and H. SACHS (*Biochem. Zeitsch.*, 1916, **76**, 359—376).—Calcium

chloride, in not too high concentrations, stimulates the hæmolysis by cobra poison of blood corpuscles which are sensitive to its influence. It can also stimulate the combined action of cobra poison and lecithin on other corpuscles, and appears to assist the fermentative action of cobra poison, which produces the scission of fatty acids from lecithin. It is not possible to state how far the action of calcium chloride is intracellular or extracellular.

The hæmolysis of non-sensitive corpuscles by cobra poison in isotonic solutions of sucrose is inhibited to a greater extent by calcium than by sodium chloride. The hæmolysis by joint action of cobra poison and lecithin in solutions of sucrose is inhibited by calcium chloride, although the hæmolysis in presence of equal quantities both in sucrose and sodium chloride solutions is stronger than in pure sodium chloride solutions. In the presence of a small amount of lecithin, calcium chloride has an inhibitory action. The action of the lecithide alone is diminished by heating, especially in more dilute solutions (in the latter case even at 37°). This diminution of action is increased by the addition of cobra poison, especially in presence of calcium salts.

The results generally confirm the conceptions of Delezenne and Ledebt, namely, that cobra poison exerts a fermentative action on lecithin, yielding a strongly hæmolytic lecithide as intermediary product; the latter undergoes, under the influence of the cobra poison, a further fermentative change to yield an end-product without hæmolytic action. Both phases of the change in lecithin are promoted by the presence of calcium salts. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

General Conceptions of Intoxication. III. The Stimulative Action of Lecithin on Ferment Formation. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **77**, 124—128. Compare A., 1916, i, 778).—The scission of urea by bacteria is not influenced by cholesterol, but is accelerated by "Agfa" lecithin; the latter substance does not, however, exert a similar influence on the urease action of soja bean. These results indicate that the lecithin stimulates the production of the ferment, but not the action of the ferment itself. S. B. S.

The Activators of Fermentation. HANS EULER and HARALD HAMMARSTEN (*Biochem. Zeitsch.*, 1916, **76**, 314—320).—It has been shown by Euler and Cassel (A., 1913, i, 1025) that the addition of ammonium formate and other substances increases the fermentation of yeast. It is now found that the formate does not also increase the amount of yeast formed. It is also found that the

addition of phosphates, which increases the rate of fermentation in acid (but not in alkaline solutions), does not cause a parallel increase in the growth of the yeast. S. B. S.

Formation of Albumin from Different Sources of Carbon. TH. BOKORNY (*Chem. Zentr.*, 1916, ii, 153; from *Münch. med. Woch.*, 1916, **63**, 791—792).—The question has been particularly studied with yeast, in the large-scale production of which the carbon nutriment is the most difficult problem. Although carbamide can serve as a source of nitrogen, its carbon is not assimilated by yeast. According to the investigations of Naegeli and others, organic acids (citric, acetic, tartaric), as well as glycerol, asparagine, peptone, mannitol, and other carbohydrates, can be used as sources of carbon for yeast, and the nature of the latter determines the utility of the different sources. Pentoses are unfermentable, but, in suitable circumstances, can serve as sources of carbon. Dextrins are scarcely fermented by yeast cultures, but readily by crude yeast. Alcohol is utilised as a source of carbon by many moulds and bacteria. The growth of many yeasts is more vigorous in alcohol than in sugar. Brewer's yeast requires the presence of sugar during cultivation because the fermentation is a protection against bacteria. The development of other moulds is checked by the rapid formation of alcohol. Attempts to replace a portion of the sugar by methyl alcohol were unsuccessful, but good results were obtained with glycerol. H. W.

Influence of Alcohol Concentration and Temperature on the Biochemical Synthesis of α-Methylgalactoside. A. AUBRY (*J. Pharm. Chim.*, 1916, [vii], **14**, 289—294. Compare A., 1914, i, 253, 498; 1916, i, 711).—Further evidence is produced in support of the view that the enzymes present in bottom yeast, causing the synthesis or hydrolysis of α-glucosides and α-galactosides respectively, are two distinct ferments. α-Galactosidase is much more resistant to the injurious influence of methyl alcohol than α-glucosidase. At the ordinary temperature the optimum alcohol concentration is between 20 and 30 grams per 100 c.c., at which concentration about 65% of the galactose present is converted into galactoside. When the alcohol concentration reaches 40 grams per 100 c.c. the enzyme is rapidly destroyed. Rise in temperature reduces the resistance of the enzyme to the influence of methyl alcohol, the maximum temperature advisable being 20—22°. W. G.

Poisoning of Enzymes in the Living Cell. HANS EULER and BETH EULER (*Chem. Zentr.*, 1916, ii, 405—406; from *Fermentforschung*, 1916, **1**, 465—470).—The authors have endeavoured to determine to what extent yeast suffers permanent damage after its fermentative power has been lessened by poison. Resorcinol has been used in the latter capacity, since that part of it which has not penetrated into the cell can be readily removed. In 0·5% solution the fermentative power of yeast is not completely destroyed

in twenty-four hours, but this effect is produced by a 2% solution; all the cells are not killed, however, since fermentation sets in to some extent when the yeast is transferred to a non-poisonous sugar solution. 0·5% Resorcinol, unlike a similar amount of toluene, does not promote the fermentation of sodium pyruvate by yeast, but it must not be assumed that resorcinol at this concentration alters to any extent the permeability of the cell membrane for the fermentable substance. The degree of poisoning probably depends on the amount of poison absorbed. The activity of yeast is increased by minute quantities of resorcinol, a maximum action being observed at a concentration of about 0·0015%. Since from solutions of resorcinol of concentration 0·5% not more than 5% of the poison disappears, it is calculated that the maximum lies at the highest at 1—2 gm.-mol. of resorcinol to 1 gm.-mol. of albumin. H. W.

The Metabolism of Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 215—218).—It is shown that the amounts of carbon, hydrogen, nitrogen, phosphorus, and inorganic elements present in the fungus diminish as the organism grows older. All elements needed for the metabolism of *Aspergillus niger* are accumulated in the young fungus material, and when this gets older they are excreted. At a certain stage, therefore, absorption of any element from the nutrient media is no longer essential for normal metabolism. S. B. S.

Catalytic Role of Potassium Nitrate in the Alcoholic Fermentation produced by Aspergillus niger. MARIN MOLLIARD (*Compt. rend.*, 1916, **163**, 570—572).—In the presence of potassium nitrate to the extent of 2 parts per 1000 of culture liquid the alcoholic fermentation produced by *Aspergillus niger* is much more prolonged and about 3·3 times more considerable than in the presence of the same amount of ammonium chloride. This increase is not due to a greater development of mycelium, nor is there any denitrification during the fermentation. The optimum amount of potassium nitrate for this process is 4 parts per 1000. W. G.

Photographic Detection of Emanations in Biological Processes. F. SCHEMINZKÝ (*Biochem. Zeit.*, 1916, **77**, 14—16).—A photographic plate is placed in a box in the bottom of which a figure is cut out (cross, etc.), and this rests on a black photographic dish, in which the various biochemical processes take place. The whole is enclosed in a dark box covered with a lid. If fermentation (yeast), germination (phaseolus), or putrefaction is allowed to take place in the black dish, the emanations pass through the figure in the box holding the plate, which on development exhibits this figure. Photographic illustrations accompany the paper. S. B. S.

Origin and Distribution of Carbamide in Nature. Application of New Methods of Estimation of Carbamide, based on the use of Xanthydrol. R. FOSSE (*Ann. Chim.*, 1916, [ix], **6**, 13—95, 155—215).—A more detailed account of work

already published (compare A., 1905, i, 541, 917; 1906, i, 687; 1912, i, 519, 541, 668, ii, 1203; 1914, i, 790, 859, ii, 154, 506, 593, 756, 757). W. G.

Some Photochemical Experiments with Pure Chlorophyll and their Bearing on Theories of Carbon Assimilation. INGVAR JÖRGENSEN and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 342—361).—Experiments were carried out with a sol of pure chlorophyll (a mixture of chlorophylls *A* and *B*) in water. On exposure to light in the presence of nitrogen, no change takes place; in the presence of carbon dioxide, chlorophyll is converted into phæophytin without any further change; no formaldehyde is produced. In the presence of oxygen, the first change is the yellowing, followed by the bleaching of the pigment. During the first stages of the change the formaldehyde production is slow, but after bleaching is complete the amount formed rapidly reaches a maximum and then diminishes. The acidity of the system increases continuously; apparently the formaldehyde undergoes oxidation in the presence of light and oxygen. The general results do not support the various hypotheses which have been suggested to explain the mechanism of carbon assimilation by green plants. S. B. S.

Selective Permeability; the Absorption of Phenol and other Solutions by the Seeds of Hordeum vulgare. ADRIAN J. BROWN and FRANK TINKER (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 373—379).—Estimations were made of the amounts of phenol, aniline, and acetic acid which enter barley seeds from solutions of varying concentration. From the results, together with those obtained from earlier investigations, the conclusion is drawn that the most strongly absorbed substances are those which give solutions having very low surface tensions. The fact that solutes giving solutions of high surface tension do not, as a rule, permeate the membrane, suggests that the selective action of the latter is due to selective adsorption. S. B. S.

Presence of Nitrites and Ammonia in Diseased Plants. Its Significance with Regard to Crop Rotation and Soil Depletion. P. A. BONCQUET (*J. Amer. Chem. Soc.*, 1916, **38**, 2572—2576).—Nitrites have not been detected in any plant tissue which was normal in the strictest sense of the word. In the case of (1) sugar beets affected with curly leaf and containing *Bacillus morulans*, (2) tobacco leaves affected with the "Mosaic Disease," and (3) potatoes infected with *Streptococcus solani*, n.sp., the juices of the leaves were always found to contain nitrites, and in some cases ammonia. The affected potato tubers only showed traces of nitrites, due to the fact that normal tubers only contain traces of nitrates. Several other plants, such as lucerne, bean, and *Malva rotundifolia*, showing abnormalities in leaf or stem structure, gave a decided nitrite reaction. It was shown that the juices obtained aseptically from all the above abnormal plants gave

abundant reduction in vitro of nitrates when inoculated in nitrite-free peptone tubes, together with a considerable bacterial growth.

In the case of a field which had been planted with potatoes for more than fifteen years, nearly every vine showed signs of nitrogen starvation due to internal bacterial reduction, although the soil was abundantly supplied with nitrates. Lack of crop rotation in this case, and also in beet fields, increases the virulence of nitrate-reducing bacteria as invaders of plant tissues, the yield of crop being reduced in some cases to such a point as to be attributed to soil depletion. W. G.

Physiological Balance of Nutrient Solutions for Plants in Sand Cultures. ARTHUR G. MCCALL (*Soil Sci.*, 1916, **2**, 207—253).—The results of sand-culture experiments with wheat manured with potassium dihydrogen phosphate, calcium nitrate, and magnesium sulphate showed that the greatest yields were obtained when the total concentration of the nutrient solutions was between 1 and 2 atmospheres of osmotic pressure.

Further experiments are described in which the effect of thirty-six different proportions of the same salts were determined, the total concentrations (1·75 atmosphere) and other conditions being the same. The results are discussed in detail and are compared with those obtained in water-cultures (J. W. Shine, *Physiol. Research*, 1915, [v], **1**, 327). The results obtained in sand-cultures correspond more nearly with those obtained in Shive's sub-optimal solution than those obtained with the optimal solution, and there was a marked difference between the solutions producing the best growth in sand- and in water-cultures.

The average ratios of calcium nitrate to magnesium sulphate in the nine best and the nine worst cultures were respectively 2·4 : 1 and 1 : 2·9. It is possible, however, that the better results were due to the increased amounts of nitrate, and not to the relation of calcium to magnesium. N. H. J. M.

The Connexion between Acid Taste and Hydrogen-Ion Concentration. THEODOR PAUL (*Ber.*, 1916, **49**, 2124—2137).—It frequently happens that a wine which is judged to be more acid to the taste than another, actually reveals less acid when titrated. If, however, the hydrogen-ion concentration is determined by, for example, studying the inversion of sucrose, then it is found that the more sour-tasting wine has the higher H-ion content. The addition of a salt with the same ion (potassium tartrate) lowers the H-ion concentration, and a wine so treated becomes less sour-tasting in proportion to the amount of tartrate added.

The details of the experiments, in which a number of professional wine-tasters participated, are fully recorded, and the number of milligram-H-ions per litre is suggested as a criterion ("acid-degree") for a wine. J. C. W.

Soluble Non-protein Nitrogen of the Soil. R. S. POTTER and R. S. SNYDER (*Chem. Zentr.*, 1916, ii, 237; from *J. Agric. Research*, **6**, 61—64).—The authors have investigated the extent

of the decomposition of organic substances in the soil by estimating the amount of soluble nitrogenous material which remains after precipitating the proteins by a suitable reagent. With this object, they have determined the nitrogen content of alkali extracts of soil with and without addition of nitrogenous substances (glutamic acid, hippuric acid, guanine, guanidine, carbamide, hypoxanthine, scatole, etc.), and, in addition, the nitrogen content of the filtrates after precipitation of the proteins from the alkali extracts by means of trichloroacetic acid. They are led to the conclusion that the alkali extracts do not contain any definite class of compounds, and that the filtrates, after removal of proteins, appear to contain the simpler nitrogenous non-protein substances. Investigation of the filtrates should therefore be a guide to the degree of decomposition of organic compounds in the soil. H. W.

Organic Phosphorus of the Soil. R. S. POTTER and T. H. BENTON (*Soil Sci.*, 1916, **2**, 291—298).—Estimations of total and organic phosphorus in alkali extracts of several soils. The method employed was a combination of those of Forbes (*Ohio Agric. Exp. Stat. Bull.*, 215) and Emmet and Grindley (*J. Amer. Chem. Soc.*, 1906, **28**, 25), both modified. The results showed that a considerable portion of the phosphorus extracted from soils is in organic forms, and that the proportion of organic to inorganic phosphorus was lowest in the soils of plots which received the more inert organic matter, such as peat and oat straw. N. H. J. M.

The Destruction of Underground Building Work by Moorland Sulphur. HANS KÜHL (*Zeitsch. angew. Chem.*, 1916, **29**, i, 335—336. Compare Thörner, A., 1916, i, 590).—Not only is the so-called 'reactive sulphur' destructive towards underground building work, but also that which occurs as sulphates of calcium and magnesium so far as cement work is concerned, for apart from the action of free sulphuric acid derived from the 'reactive sulphur,' the above soluble sulphates by penetrating into the cement give rise to the formation of a voluminous, almost insoluble double compound of calcium aluminate and calcium sulphate, $3CaO,Al_2O_3,3CaSO_4$, a reaction overlooked by Thörner (*loc. cit.*). Consequently, soluble sulphates must have a similar corrosive action on the cement to that of free sulphuric acid. G. F. M.

Nature of the Sulphur of Peat Soils. WILH. THÖRNER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 363—364. Compare A., 1916, i, 590). —A reply to Kühl (preceding abstract). Calcium and magnesium sulphates occur in most peat soils only in small amounts; exceptions occur in soils near the sea owing, probably, to the presence of considerable amounts of these salts in the soil water. This water may, undoubtedly cause injury to the foundations of buildings.

Under ordinary conditions the sulphates present in peat are not injurious to vegetation or to buildings. N. H. J. M.

Organic Chemistry

Production of the Lower Chlorides of Methane from Natural Gas. CLAYTON W. BEDFORD (*J. Ind. Eng. Chem.*, 1910, **8**, 1090—1094).—By subjecting a mixture of chlorine and natural gas, in a chamber containing blocks of ice, to the action of light from the white-flame arc, a heavy liquid was obtained beneath the water produced by the melted ice; this liquid consisted of methylene chloride, 35%; chloroform, 35%; carbon tetrachloride, 5%; and ethane chloro-derivatives, 20%. A portion of the product, amounting to about 14% of the total, remained soluble in the water, and consisted of methylene chloride, 61%; chloroform, 28%; carbon tetrachloride, 1·5%; and ethane chloro-derivatives, 6%. Two hundred and fifty cubic feet of the natural gas yielded several gallons of the mixed chlorides. W. P. S.

Preparation of Carbon Tetrachloride. THE DOW CHEMICAL Co. (U.S. Pat., 1204608; from *J. Soc. Chem. Ind.,* 1916, **35**, 1271—1272).—Carbon tetrachloride is prepared by the action of carbon disulphide on sulphur dichloride in such quantity that the latter is reduced practically to the monochloride; the temperature is then raised and more carbon disulphide added until the monochloride is reduced to sulphur. The process may be modified by carrying on the first stage until the residue consists of a hot solution of sulphur in sulphur monochloride, adding more sulphur dichloride, and continuing the addition of carbon disulphide until the same point is reached again, and finally raising the temperature and adding carbon disulphide until the residue, which is kept liquid, consists mainly of sulphur. The carbon tetrachloride evolved in the reactions is condensed. H. W.

Preparation of β-Chloro*iso*pentane. BADISCHE ANILIN- & SODA-FABRIK (U.S. Pat., 1202282; from *J. Soc. Chem. Ind.*, 1916, **35**, 1235).—A mixture of petrol hydrocarbons, chiefly pentane and *iso*pentane, is chlorinated; hydrogen chloride is eliminated from the separated monochloropentanes by a suitable reagent, and the olefines obtained are treated with hydrogen chloride. The β-chloro*iso*pentane thus formed is separated, the residue treated with an isomerising agent, and more β-chloro*iso*pentane produced by the action of hydrogen chloride. The processes of separation, isomerisation, and treatment with hydrogen chloride may be repeated until practically the whole of the olefine is converted into β-chloro*iso*pentane. H. W.

Derivatives of Trihalogeno-*tert.*-butyl Alcohols. I. The Acetic Ester of Tribromo-*tert.*-butyl Alcohol or Brometone Acetic Ester. T. B. ALDRICH and C. P. BECKWITH (*J. Amer. Chem. Soc.*, 1916, **38**, 2740—2746. Compare A., 1916, i, 115).—β-Tri-

bromomethylpropan-β-ol, $CBr_3\cdot CMe_2\cdot OH$, is converted into the corresponding *acetate*, $CBr_3\cdot CMe_2\cdot OAc$, a white solid, m. p. 43—44°, by heating it either with a mixture of acetic anhydride and sodium acetate for two hours, or with acetyl chloride or bromide in acetic acid solution. In its properties, the acetate resembles the corresponding chloro-compound (*loc. cit.*). It is somewhat similar to chloretone in its pharmacological action, but its action is weaker and less rapid than that of chloretone.

W. G.

The Constituents of Wool Fat. F. RÖHMANN (*Biochem. Zeitsch.*, 1916, **77**, 298—328).—A detailed account is given of attempts to separate the constituents of wool fat. As a result of the experiments, the author draws the conclusion that wool fat consists of a mixture of the esters of cholesterol and of alcohols of the fatty series, including ceryl alcohol and alcohols with a smaller number of carbon atoms. He was unable to confirm the presence of carnaubyl alcohol or of *iso*cholesterol. The fatty acids are apparently cerotic, palmitic, and stearic acids in the more solid constituents of the fat. The more liquid constituents of the fat contain, in addition to free cholesterol, a mixture of alcohols of an oily nature, and the fatty acids are probably stearic and palmitic acids, and an optically active acid (hydroxystearic acid?), together with resin acids. From the more solid constituents of the fat there was found, in addition, mixed with the fatty acids, a substance, m. p. 103°, which may be the anhydride of lanoceric acid. Carnaubic acid, which has been described as a constituent of wool fat, is regarded by the author as a mixture of cerotic acid with acids containing a smaller number of carbon atoms. S. B. S.

Esters of Oleic Acid and their Hydrogenated Products. CARLETON ELLIS and LOUIS RABINOVITZ (*J. Ind. Eng. Chem.*, 1916, **8**, 1105—1108).—The methyl, ethyl, propyl, *iso*butyl, amyl, benzyl, and glyceryl esters of oleic acid were prepared; they were oily liquids at the ordinary temperature. These esters, when hydrogenated in the presence of reduced nickel, yielded products which were practically saturated. The nature of the alcohol did not seem to affect to any great extent the rate or degree of hydrogenation. A substance, prepared by heating oleic acid with aniline, hydrogenated readily, and yielded a hard, brittle mass, m. p. 76°. W. P. S.

Solubility of Alkali Oxalates in the Presence of some Alkali Salts. A. COLANI (*Bull. Soc. chim.*, 1916, [iv], **19**, 405—407).—The author has determined the solubility of potassium oxalate in the presence of potassium chloride, potassium sulphate, or potassium nitrate, and the solubilities of sodium and ammonium oxalates in the presence of the corresponding sodium and ammonium salts at 15° and 50°, the solutions being saturated with respect to the two solid phases. The results are tabulated.

W. G.

Variations of the Rotatory Power of Galactose and Dextrose in Propyl Alcohol at Different Concentrations. D. FOULKES (*J. Pharm. Chim.*, 1916, [vii], **14**, 364—366).—The rotatory power of galactose diminishes, and of dextrose increases, as the solution becomes richer in propyl alcohol. W. G.

The Optical Rotation and Cryoscopic Behaviour of Sugars Dissolved in (*a*) Formamide, (*b*) Water. II. JOHN EDWIN MACKENZIE and SUDHAMOY GHOSH (*Proc. Roy. Soc. Edin.*, 1916, **36**, iii, 204—215).—The authors have now extended their work (compare A., 1915, ii, 301) to a study of β-*d*-glucose, β-*d*-galactose, and maltose. Molecular-weight determinations gave no indication of association of the sugar molecule. The mutarotation in formamide solution has now been measured, starting from both the α- and β-forms of *d*-glucose, *d*-galactose, and lactose. As in the case of the aqueous solutions of these sugars, the constant rotation shown where there is equilibrium between the two modifications is found to be the same whether the starting point be the α- or the β-modification. The authors suggest that the mechanism of mutarotation may be due to the formation of a compound, such as is known in the case of β-glucose and pyridine, and subsequent splitting off of the pyridine or formamide molecule, with formation of α- and β-forms. W. G.

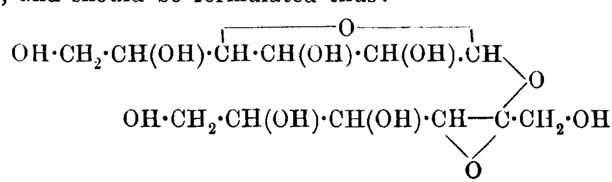
Evidence Indicating the Existence of a New Variety of Fructose. A Reactive Form of Methylfructoside. JAMES COLQUHOUN IRVINE and GEORGE ROBERTSON (T., 1916, **109**, 1305—1314).—It has been shown that glucose can exist not only as the ordinary α- and β-isomerides of a butylene oxide type, but also as highly reactive "γ-glucose," which is probably analogous to ethylene oxide (A., 1915, i, 381). The idea naturally occurs that other hexoses may also conform to this "γ-glucose" type, and a review of the literature shows that a large number of facts are known which are not explained by butylene oxide formulations. Notably, the extreme ease with which sucrose is hydrolysed would suggest that either the glucose or fructose fragment in it conforms to γ-glucose. It has been proved, however, that the glucose fragment is present identically as it is in α-methylglucoside (T., 1905, **87**, 1022), from which it naturally follows that the fructose may have the γ-glucose structure, and, consequently, that the prevailing formula for sucrose needs to be corrected (see Haworth and Law, next page).

An examination of the methylfructosides has now revealed the existence of a type corresponding with γ-methylglucoside, which therefore probably contains the ethylene–oxide ring. This reacts so readily with acetone to form *methylfructosidemonoacetone*, $C_{10}H_{18}O_6$, a vitreous mass, b. p. 142—145°/0·05 mm., that even the trace of acetone commonly present in methyl alcohol is involved in this condensation during the production of the methylfructosides. Much that was obscure in previous work on the changes in rotation which result when fructose is condensed with

methyl alcohol can therefore be explained. At least four methylfructosides are formed, the stereoisomeric α- and β-forms of the butylene oxide type and the α- and β-forms of the ethylene oxide type, and the condensation of these with the traces of acetone still further complicates matters. J. C. W.

The Sublimation of Sugars. SUDHAMOY GHOSH (*Proc. Roy. Soc. Edin.*, 1916, **36**, iii, 216—218).—Rhamnose or its hydrate, when heated at 105° under a pressure of 1—2 mm., sublimes slowly, and the sublimate obtained has all the physical properties of anhydrous rhamnose, and gives the same phenylosazone. At from 1—2 mm. pressure and about 100°, lævulose also sublimes, but much less rapidly than rhamnose. W. G.

Constitution of the Disaccharides. I. Structure of Sucrose. WALTER NORMAN HAWORTH and JAMES LAW (T., 1916, **109**, 1314—1325).—When octamethylsucrose is hydrolysed by means of hydrochloric acid, the rotation only changes from $[\alpha]_D +66 \cdot 7°$ to $+57°$, whereas a mixture of the known crystalline tetramethylglucose and tetramethylfructose would be lævorotatory, like invert-sugar. Purdie and Paul, however, have shown that an oily, dextrorotatory tetramethylfructose can be obtained (T., 1907, **91**, 294), and reasons are now given for assuming that this belongs to the type of γ-fructose, that is, it contains in all probability an ethylene–oxide structure. It follows, therefore, since the glucose fragment is of the normal type (crystalline tetramethylglucose can be isolated), that the abnormal rotation must be due to the new γ-fructose form, that is, that when octamethylsucrose is hydrolysed, it yields the α- and β-forms of butylene–oxidic tetramethylglucose and the α- and β-forms of ethylene–oxidic tetramethylfructose. Consequently, the original sucrose contains the ethylene–oxidic fructose, and should be formulated thus:



The hydrolysis of sucrose can therefore no longer be regarded as a very simple process, for it may involve the production of the α- and β-forms of butylene–oxidic glucose and ethylene–oxidic fructose, and then the change of these into the more stable α- and β-butylene–oxidic fructoses. J. C. W.

The Consistency of Pectin Gels. JAS. B. MCNAIR (*J. Physical Chem.*, 1916, **20**, 633—639).—The active substances concerned in the preparation of fruit jellies are supposed to be pectin, sucrose, and acid. The behaviour of solutions containing the two first-mentioned substances and citric acid has been examined, and it is found that jellies may be obtained when the concentrations are

suitably chosen. Jellies are also formed in the absence of the acid, but the pectin concentration required is considerably greater.

H. M. D.

Influence of Acid Radicles Containing Different Secondary Alkyls on the Narcotic Action of Urethane. ISAO ODAIRA (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 319—340).—The author has synthesised a number of derivatives of urethane, and examined their physiological activities.

α-Ethylbutyrylurethane ("*detonal*"), $CHEt_2 \cdot CO \cdot NH \cdot CO_2Et$, from urethane and the acyl chloride, forms colourless needles, m. p. 88°; *α-ethylvalerylurethane* ("*epronal*"), $CHEtPr \cdot CO \cdot NH \cdot CO_2Et$, has m. p. 72°; *α-propylvalerylurethane* ("*dipronal*") has m. p. 88—89°; *α-propylhexoylurethane* ("*probnal*") has m. p. 69—70°; *α-butylhexoylurethane* ("*dibnal*") has m. p. 44°. The solubilities of these compounds in cold water decreases with increasing molecular weight. n-*Heptoylurethane* crystallises in thin plates, m. p. 67°; iso*amylurethane*, $CHEt_2 \cdot NH \cdot CO_2Et$, is a colourless, fragrant oil, b. p. 155° (460 mm.); *α-bromo-α-ethylvalerylcarbamide*, $CBrEtPr \cdot CO \cdot NH \cdot CO \cdot NH_2$, forms an opaque liquid at 97°, which is clear at 105°.

Physiological experiments are described in which these compounds are compared with urethane and other common narcotics. It appears that the secondary alkyl group has a greater modifying influence than the primary alkyl, and that the narcotic activity is enhanced by lengthening the chain in the substituent. The acyl group as such has not much influence on the narcotic power, but diminishes the toxicity of the urethanes.

It has been suggested that the narcotic effect of a substance depends on the coefficient of its distribution between oil and water. The partition coefficients of some of these drugs have been determined for olive oil and water, and it is found that, whilst they do not harmonise with the duration of the narcosis, the promptitude with which the substance acts is the more the higher its coefficient.

The paper is illustrated by a blood-pressure curve for a rabbit under the influence of "epronal," which shows that the vagus and respiratory centre are uninfluenced.

J. C. W.

The Synthesis of Amino-Acids. α-Amino-γδ-dihydroxyvaleric Acid; γ-Hydroxyproline; αδ-Diamino-γ-hydroxyvaleric Acid. EINAR HAMMARSTEN (*Compt. rend. Lab. Carlsberg*, 1916, **11**, 223—262).—Allylhippuric acid (compare Sørensen, this vol., i, 89) gives an *ethyl* ester, m. p. 54·5°, which when brominated in chloroform solution yields *ethyl γδ-dibromo-α-benzoylaminovaleric acid*, $CH_2Br \cdot CHBr \cdot CH_2 \cdot CH(NHBz) \cdot CO_2Et$, m. p. 96·5—97·5°. The corresponding acid was obtained in the solid state, m. p. 203—204° (compare Sørensen, A., 1908, i, 981), as was δ-bromo-α-benzoylamino-γ-valerolactone, m. p. 162·5—163°, when the dibromo-acid was boiled with water or acted on in cold alcoholic solution with aqueous barium hydroxide. This lactone, on further

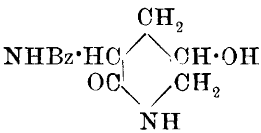
treatment with barium hydroxide, yielded *α-benzoylamino-δ-hydroxyvalerolactone*, m. p. 167—168°, which when heated on a water-bath with concentrated hydrochloric acid gave *α-amino-δ-hydroxy-γ-valerolactone hydrochloride*,

$$OH\cdot CH_2\cdot CH<\begin{matrix}O\text{---}CO\\ CH_2\cdot CH\cdot NH_2,HCl\end{matrix},$$

m. p. 189—193°. From this hydrochloride, α-amino-γδ-dihydroxyvaleric acid was obtained in the form of its copper salt (compare Fischer and Krämer, A., 1908, i, 858).

The filtrate from the preparation of δ-bromo-α-benzoylamino-γ-valerolactone gave *4-benzoyloxyproline*, m. p. 158—161°, which was first isolated in the form of its *copper* salt. From this benzoylated proline, the two copper salts of 4-hydroxyproline were prepared by boiling it in aqueous solution with copper carbonate, after first boiling it with a saturated solution of barium hydroxide.

When a solution of δ-bromo-α-benzoylamino-γ-valerolactone in absolute alcohol is saturated with ammonia, *3-benzoylamino-5-hydroxypiperidone* (annexed formula) is obtained, m. p. 225—226°, and this when heated with saturated aqueous barium hydroxide, gives γ-hydroxy-α-benzoylornithine, m. p. 255—256°, of which a *monopicrate*, m. p. 185—190° (compare Kossel and Weiss, A., 1910, ii, 909), and a *platinichloride* were prepared. W. G.



Preparation of Cyanamide from Calcium Cyanamide. EMIL ALPHONSE WERNER (T., 1916, **109**, 1325—1327).—Calcium cyanamide is thoroughly kneaded with a little more 50% acetic acid than is required for neutralisation, the paste is exposed to the air for a day until it becomes a dry powder, anhydrous sodium acetate or pumice powder being added if necessary, and then the free cyanamide is extracted with ether. The yield is about 95% of the theoretical. J. C. W.

Some Reactions Produced by Mercuric Iodide. ERNALD GEORGE JUSTINIAN HARTLEY (T., 1916, **109**, 1302—1305).—Mercuric iodide and acetonitrile do not react when heated together at 100° (compare following abstract), but when methyl iodide is added to the reaction mixture, combination takes place between the three substances, a dark brown, viscous oil being produced. The reaction appears to be a general one, since acetonitrile may be replaced by propionitrile, benzonitrile, phenylacetonitrile, and β-naphthonitrile. The product appears to be the mercuric iodide of a quaternary base, since when iodine is removed as silver iodide from the acetone solution, and the mercury and excess of silver removed by hydrogen sulphide, a yellow solution of the salt of the base is obtained. No crystalline salts could be obtained, but the addition of sodium hydroxide to the solutions liberates the base as an oil possessing

a strongly alkaline reaction. Various precipitation reactions of solutions of these salts are described.

The mercury compounds could not be obtained pure, but analyses point to one of the two following formulæ: $HgI_2,2RCN,R'I$ or $HgI_2,3RCN,R'I$.

The influence of mercuric iodide in promoting the above reactions has led the author to investigate other reactions. It is found that although no reaction takes place between β-tetramethyl ferrocyanide and methyl iodide when heated at 100° (compare T., 1913, **103**, 1199), the addition of mercuric iodide leads to the formation of a mercuri-iodide of hexamethyl ferrocyanogen. T. S. P.

The Reaction between Methyl Iodide and some Metallic Cyanides. Ernald George Justinian Hartley (T., 1916, **109**, 1296—1301).—As a result of a fuller examination of the reaction between silver cyanide and methyl iodide (compare Wade, T., 1902, **81**, 1608), it is found that these two substances combine slowly at the ordinary laboratory temperature, giving a crystalline compound of the formula $(AgNC)_2,CH_3I$. At a temperature of about 40°, a further molecule of methyl iodide is taken up, and the compound $AgNC,CH_3I$, or perhaps $(AgNC,CH_3I)_2$, is formed. Potassium argenticyanide does not react with methyl iodide. The compounds above-mentioned readily undergo decomposition, with the formation of silver iodide and methylcarbylamine.

According to the author, the formulation of potassium argenticyanide and silver cyanide as $K\cdot N\vdots C\vdots N{<}^{C}_{Ag}$ and $Ag\cdot N\vdots C\vdots N{<}^{C}_{Ag}$ respectively accounts for the observed phenomena. In the case of silver cyanide, the addition of methyl iodide takes place according to the scheme: $Ag\cdot\overset{CH_3}{\underset{I}{N}}\vdots C\vdots N{<}^{C}_{Ag}$, which at higher temperatures gives the group $Ag\cdot\overset{CH_3}{\underset{I}{N}}\vdots C$, leaving the unsaturated residue $Ag\cdot\ddot{N}\vdots C$ to combine further with methyl iodide. In the case of potassium argenticyanide, no addition of CH_3I can take place, since the free valencies both of the carbon and nitrogen atoms are no longer available.

When mercuric cyanide and methyl iodide are heated at 110°, a black, tarry, amorphous substance is produced, which cannot be purified. Judging from the weights of the reacting substances, the amorphous substance is the compound $(CH_3NC)_2,HgI_2$. It can also be obtained by the interaction of mercuric iodide and methylcarbylamine; acetonitrile does not react with methyl iodide.

T. S. P.

Isomerisation Phenomena of the Three-membered Ring. N. A. ROZANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 168—189).—The author has prepared ethyl*cyclo*propane and investigated its transformations. Acetyl*cyclo*propane, prepared from ethyl acetoacetate by way of acetylpropyl alcohol (compare Lipp, A., 1889, 843), was converted into the hydrazone,

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>CH\cdot CMe{:}N\cdot NH_2,$$

b. p. 63·5°/5—6 mm., D_4^{20} 0·9663, n_D^{20} 1·50265. The action of fused potassium hydroxide on the hydrazone in presence of platinised porous tile in a silver tube sealed inside a glass tube at 240—250° yields ethyl*cyclo*propane, b. p. 36—36·5°/750 mm., D_4^{20} 0·6832, n_D^{20} 1·37914 (compare Demjanov and Dojarenko, A., 1913, i, 451; Zelinski and Schtscherbak, A., 1913, i, 254).

When ethyl*cyclo*propane is shaken in a sealed tube at 0° with fuming hydrobromic acid, it is converted into *γ-bromopentane*, $CHEt_2Br$, b. p. 118·5—119·5°/745 mm., D_4^{20} 1·2171, n_D^{20} 1·44299, which, when heated with water in a sealed tube at 100°, gives Δ^{β}-pentene and a secondary alcohol. With bromine in direct sunlight, ethyl*cyclo*propane yields: (1) γ-bromopentane, which is a secondary product; (2) *αγ-dibromopentane*, $CH_2Br\cdot CH_2\cdot CHEtBr$, b. p. 190—195°/750 mm., D_4^{20} 1·6721, n_D^{20} 1·50482; and (3) apparently a solution of the tetrabromo- in the dibromo-compound. By fuming hydriodic acid it is converted into γ-iodopentane, and the action on it of sulphuric acid diluted with one-half its volume of water gives diethylcarbinol; with dilute nitric acid (D 1·075) it yields ethylmalonic acid.

When passed through a tube containing asbestos and alumina at 300—310°, ethyl*cyclo*propane undergoes isomerisation into Δ^{β}-pentene. Reduction of ethyl*cyclo*propane by either Sabatier's or Ipatiev's method readily yields β-methylbutane. In *cyclo*propane derivatives containing oxygen in one state or another in the side-chain, the trimethylene ring is, however, much more stable, and persists unbroken in the reduction products; thus, reduction of acetyl*cyclo*propane by Ipatiev's method yields *cyclo*propylmethylcarbinol (compare Michiels, A., 1912, i, 259; Demjanov and Pinegin, A., 1914, i, 527).

The ultra-violet absorption spectra of Δ^{β}-pentene, ethyl*cyclo*propane, β-methylbutane, and *n*-pentane have been investigated. The general absorption of all these hydrocarbons is very weak, and with the unsaturated compounds the absorption is displaced towards the visible part of the spectrum. T. H. P.

Oxidation of *o*-Iodotoluene with Potassium Permanganate. P. J. MONTAGNE (*Chem. Weekblad*, 1916, **13**, 1294—1296).—Potassium permanganate oxidises *o*-iodotoluene to a mixture of *o*-iodosobenzoic acid (3 parts) and *o*-iodobenzoic acid (1 part); the iodoso-compound is insoluble in ether. A. J. W.

Additive Compounds of Trinitrobenzene. JOHN JOSEPH SUDBOROUGH (T., 1916, **109**, 1339—1348).—In continuation of a study on the additive capacity of polynitro-aromatic compounds

(T., 1901—1911), an account is now given of a large number of compounds of *s*-trinitrobenzene with aromatic hydrocarbons, substitution products of naphthalene, cyclic bases, benzene derivatives, and aromatic sulphur compounds. The hydrocarbons form fairly stable compounds, as they do with picric acid. These are usually yellow, whilst the amines and phenols give more deeply coloured, and frequently more stable, products. It appears, therefore, that the union is due to the latent valencies of the nitro-groups on the one hand and the aromatic nuclei on the other, any hydroxyl, alkyl, keto-, amino-, or alkylamino-groups acting merely as auxochromes and also conferring additional stability on the products. The number of molecules of trinitrobenzene with which one of the molecules combines seems to depend chiefly on the number of aromatic nuclei in the latter, condensed rings acting as one nucleus. Thus compounds like naphthalene, naphthols, quinoline, etc., unite with one molecular proportion of trinitrobenzene; diphenylethane, stilbene, diphenylamine, etc., with two. There are, however, notable exceptions to these generalisations. In some cases the ratio is 1 : 0·5; in the case of fluorene it is 1 : 1·5. Reference is also made to the auxochromic effect of amino- and hydroxy-groups and ethylene linkings. J. C. W.

Additive Compounds of *s*-Trinitrobenzene with Amino-derivatives of Complex Aromatic Hydrocarbons. SHUNKER TRIMBAK CADRE and JOHN JOSEPH SUDBOROUGH (T., 1916, **109**, 1349—1354).—As a rule, naphthalene derivatives give more stable additive compounds with trinitrobenzene than the corresponding benzene derivatives. The question therefore arises whether derivatives of still more complex hydrocarbons form still more stable compounds. The behaviour of trinitrobenzene towards 2-, 4-, and 9-aminophenanthrenes, 9-aminoanthracene, the anthramines, the anthrols and their ethyl ethers, 2-aminofluorene, diaminofluorene, and 9-aminoacenaphthene has therefore been examined. Additive compounds of a fair degree of stability are formed in all cases, mostly equimolecular in composition. They are more highly coloured than those of the corresponding naphthalene derivatives, the amines giving brown to black crystals and the hydroxy-compounds reddish-brown. Full descriptions of the substances are given. J. C. W.

The Sixth (η-) Trinitrotoluene and the Corresponding Halogenated Dinitro-substitution Products. W. KÖRNER and A. CONTARDI (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339—348. Compare A., 1915, i, 790, 875).—The authors have now prepared the last of the trinitrotoluenes, namely, the 2 : 3 : 6-compound, by the following series of transformations: 2 : 4 : 6-trinitrotoluene $\longrightarrow$ 2 : 6-dinitro-*p*-toluidine $\longrightarrow$ 3-bromo-2 : 6-dinitro-*p*-toluidine $\longrightarrow$ 3-bromo-2 : 6-dinitrotoluene $\longrightarrow$ 2 : 6-dinitro-*m*-toluidine $\longrightarrow$ 2 : 3 : 6-trinitrotoluene. Conditions have been found under which 2 : 4 : 6-trinitrotoluene gives a 60% yield of 2 : 6-dinitro-*p*-toluidine; this reaction, and the secondary products of the reduction, are to be dealt with in detail in a later paper.

2 : 6-*Dinitroaceto*-p-*toluidide*, $NHAc\cdot C_6H_2Me(NO_2)_2$, forms slender, white needles, m. p. 223°.

3-*Bromo*-2 : 6-*dinitro*-p-*toluidine*, $NH_2\cdot C_6HMeBr(NO_2)_2$, formed, together with a little 3 : 5-dibromo-2 : 6-dinitro-*p*-toluidine (*vide infra*), by the action of bromine on the dinitrotoluidine in presence of sodium acetate and acetic acid, crystallises in shining, pale yellow prisms or short needles, m. p. 174°. By means of the diazo-reaction, it may be converted into 3-bromo-2 : 4 : 6-trinitrotoluene (compare Bentley and Warren, A., 1890, 485).

3-*Bromo*-2 : 6-*dinitroaceto*-p-*toluidide*, $NHAc\cdot C_6HMeBr(NO_2)_2$, crystallises in almost colourless plates, m. p. 151°.

3 : 5-*Dibromo*-2 : 6-*dinitro*-p-*toluidine*, $NH_2\cdot C_6MeBr_2(NO_2)_2$, obtained by further bromination of the corresponding 3-monobromo-derivative (see above), forms shining, pale yellow prisms, m. p. 177°.

3 : 5-*Dibromo*-2 : 6-*dinitrotoluene*, $C_6HMeBr_2(NO_2)_2$, prepared by treating an absolute alcoholic solution of the previous compound with ethyl nitrite at an excess pressure of about 0·5 atmo., forms shining, white needles or flat plates, m. p. 120°.

3 : 5-Dibromo-2 : 4 : 6-trinitrotoluene, obtained by the action of nitrous vapours at 0° on a suspension of finely powdered 3 : 5-dibromo-2 : 6-dinitro-*p*-toluidine in concentrated nitric acid, forms flat, white needles, m. p. 240°; Palmer (A., 1889, 390) described this as a yellow product, m. p. 229—230°.

2 : 6-*Dinitro*-m-*toluidine*, $NH_2\cdot C_6H_2Me(NO_2)_2$, prepared by the action of 10% alcoholic ammonia solution on 3-bromo-2 : 6-dinitrotoluene (see below) at 145°, forms shining, pale yellow prisms or needles, m. p. 133·8°.

2 : 6-*Dinitroaceto*-m-*toluidide*, $NHAc\cdot C_6H_2Me(NO_2)_2$, forms shining, thin, colourless plates or large prisms, m. p. 166°.

2 : 3 : 6-*Trinitrotoluene* (η-), formed from 2 : 6-dinitro-*m*-toluidine by way of the diazo-nitrate, crystallises in shining, white needles, belonging to the prismatic class of the monoclinic system [ARTINI : $a : b : c = 1·8362 : 1 : 0·3493$; $\beta = 56°39·5'$], m. p. 111°. By treatment with alcoholic ammonia in a closed tube at 110—120°, it is converted into (1) 3 : 6-dinitro-*o*-toluidine, m. p. 151°, to be described later, and (2) a substance which crystallises in plastic, orange-yellow, flat needles, m. p. 128°, remains unchanged in appearance and melting point after several crystallisations, and is a mixture containing at least 3 : 6-dinitro-*o*-toluidine and 2 : 6-dinitro-*m*-toluidine.

3-*Chloro*-2 : 6-*dinitrotoluene*, $C_6H_2MeCl(NO_2)_2$, forms large, almost colourless, shining prisms, m. p. 75°.

3-*Bromo*-2 : 6-*dinitrotoluene*, $C_7H_5O_4N_2Br$, forms slender, white prisms or large prisms, m. p. 86·2°.

3-*Iodo*-2 : 6-*dinitrotoluene*, $C_7H_5O_4N_2I$, forms large aggregates of small, shining, colourless plates, m. p. 90°.

2 : 3 : 6-*Trinitrobenzoic acid*, $C_6H_2(NO_2)_3\cdot CO_2H$, obtained by oxidising 2 : 3 : 6-trinitrotoluene with sulphuric and chromic acids, forms slender, white needles, m. p. 55° ($+2H_2O$) or 160° (anhydrous).

T. H. P.

Preparation of 4 - Nitro - 2 - aminobenzenesulphonic [3-Nitrosulphanilic] Acid. FARBENFABR. VORM. F. BAYER & Co. (D.R.-P., 294547; from *J. Soc. Chem. Ind.*, 1916, **35**, 1213).—*m*-Nitroaniline is sulphonated at 120—140° with the calculated quantity or a slight excess of fuming sulphuric acid, and the product is cooled and stirred with water. The precipitated sulphonic acid is filtered and washed, and may be purified by means of its sparingly soluble sodium salt. H. W.

The Beckmann Rearrangement. VI. The Rate of Rearrangement of Phenylmethylketoxime by Different Acid Chlorides, the Spontaneous Rearrangement of its Benzenesulphonic Ester, and the Synthesis of Phenylacetimino Benzenesulphonate. MITSURU KUHARA and HIKOHEI WATANABE (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 349—353. Compare A., 1915, i, 143).—As in the case of benzophenone-oxime, so with the oxime of acetophenone, the chlorides of the stronger acids effect rearrangement more quickly than those of the weaker acids. The yield of acetanilide obtained by heating the oxime with acyl chlorides is found to vary, for example, from only 39% at the end of six hours with acetyl chloride to 98·8% during half an hour with oenzenesulphonyl chloride.

Correspondingly, *phenylmethylketoxime benzenesulphonate*,

$$SO_2Ph\cdot O\cdot N:CPhMe,$$

colourless needles, m. p. 60—61°, spontaneously changes into a viscous oil in a few days in the cold, quickly in ultra-violet light, or with violence at 81—82°. This oil is *phenylacetimino benzenesulphonate*, $SO_2Ph\cdot O\cdot CMe:NPh$, which may also be prepared by the interaction of phenylacetimino chloride and silver benzenesulphonate. J. C. W.

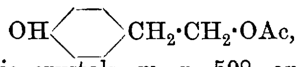
The Beckmann Rearrangement. VII. The Rearrangement of Ethyl*syn*benzhydroximic Acid, the Different Acid Chlorides, and its Benzenesulphonic Ester. MITSURU KUHARA and FUSAO ISHIKAWA (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 655—360).—Ethyl*syn*benzhydroximic acid follows the same rule as the ketoximes, namely, that the chlorides of stronger acids bring about its rearrangement more readily than those of weak acids. The *benzenesulphonate*, $SO_2Ph\cdot O\cdot N:CPh\cdot OEt$, has m. p. 54—55°, and decomposes on heating, violently at 150°, into phenylcarbmide and ethyl benzenesulphonate. The expected intermediate product, *ethoxyphenyliminomethyl benzenesulphonate*,

$$SO_2Ph\cdot O\cdot C(OEt):NPh,$$

s therefore unstable at higher temperatures, but it can be isolated s an oil if the original oxime is warmed with benzenesulphonyl hloride in dry pyridine. J. C. W.

Biological Syntheses: *p*-Hydroxyphenylethanol (Tyrool). P. S. PISCHTSCHIMUKA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, —54). The greater part of this paper has been already pubished (compare A., 1912, ii, 590; Ehrlich and Pischtschimuka, A., 912, i, 853).

The formation of esters during the normal alcoholic fermentation of amino-acids appears to be a biological process of wide extent, its object being the union of the excess of acids and alcohols, which would be injurious to the micro-organisms. A number of the esters of tyrosol have now been prepared by ordinary chemical synthetical methods, and are found to exhibit faint odours at the most. The mixture of esters formed naturally during alcoholic fermentation has a pleasant odour, but this is probably due to the presence of admixed indole derivatives. The following esters have been prepared.

The *monoacetate*, , forms thick, pris matic, non-hygroscopic crystals, m. p. 59°, and is very sparingly soluble in cold water, although the solution gives Millon's reaction The *diacetate*, $OAc\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OAc$, forms a transparent colourless, viscous oil, b. p. 187°/18 mm., solidifying to a vitreous mass at the temperature of liquid air; it is almost insoluble in water, but the aqueous solution gives Millon's reaction. The *mono*iso*valerate*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH_2\cdot CHMe_2$, forms a colourless, oily liquid, b. p. 208·5°/18 mm., with a faint, aromati odour. The *di*iso*valerate*, $C_{18}H_{26}O_4$, is a liquid, b. p. 228°/18 mm. resembling the mono*iso*valerate, and forms a stable emulsion with water. The *monoformate*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot O\cdot CHO$, does no distil even at 12 mm. pressure, and does not crystallise. The *succinate*, $(OH\cdot C_6H_4\cdot CH_2\cdot CH_2)_2C_4H_4O_4$, crystallises in slende needles, m. p. 116°. The *hydrogen succinate*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2\cdot C_2H_4\cdot CO_2H,$$

forms crystals, m. p. 106°, gives an intense Millon's reaction, an has an acid reaction towards phenolphthalein. The *tartrate* $(OH\cdot C_6H_4\cdot CH_2\cdot CH_2)_2C_4H_4O_6$, forms colourless, prismatic aggre gates, m. p. 143°. The *hydrogen tartrate*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2\cdot [CH(OH)]_2\cdot CO_2H,$$

forms crystals, m. p. 162°, is comparatively stable towards water and yields a crystalline *sodium* salt. T. H. P.

Esterification. VIII. The Esterification of Benzoi Acid by Isomeric Butyl Mercaptans. J. W. Kimball an E. Emmet Reid (*J. Amer. Chem. Soc.*, 1916, **38**, 2757—2768).- The four isomeric butyl thiolbenzoates were prepared by the actic of the corresponding butyl bromide on the potassium salt of thic benzoic acid. n-*Butyl thiolbenzoate* has b. p. 160°/23 mm D_{25}^{25} 1·0514; iso*butyl thiolbenzoate*, b. p. 150°/20 mm., D_{25}^{25} 1·0457 sec.-*butyl thiolbenzoate*, b. p. 151°/23 mm., D_{25}^{25} 1·0488; and ter *butyl thiolbenzoate*, b. p. 110°/28 mm., D_{25}^{25} 1·0468.

The authors have determined the rates and limits of esterific tion of benzoic acid by normal, *iso*-, and *sec.*-butyl mercaptans 200°, and also the limits for the saponification of the four but thiolbenzoates at the same temperature. In the esterifications, tl rates and limits for the normal and *iso*-mercaptans were found be practically the same, those for the secondary mercaptans being much lower. In every case the limits were much lower than the

for the corresponding alcohols, and were independent of the relative amounts of acid and mercaptan used. The saponification of the esters was found to be very irregular and unsatisfactory on account of the immiscibility of the ester and water and the decomposition of the esters, particularly in the case of *tert.*-butyl thiolbenzoate. W. G.

Esterification. VII. The Esterification of *o*-, *m*-, **and** *p*-**Toluic Acids by Ethyl Mercaptan.** J. H. SACHS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2746—2757).—A quantitative study of the esterification of the three toluic acids by ethyl mercaptan and of the hydrolysis of ethyl *o*- and *p*-thioltoluates by water.

o-*Thioltoluic acid*, b. p. 133°/35 mm., D_{25}^{25} 1·1451, was obtained in the form of its *potassium* salt by adding *o*-toluoyl chloride to an alcoholic solution of potassium hydroxide saturated with hydrogen sulphide. The potassium salt when alkylated with ethyl bromide gave *ethyl* o-*thioltoluate*, $C_6H_4Me\cdot CO\cdot SEt$, b. p. 133°/15 mm., D_{25}^{25} 1·0513. p-*Thioltoluic acid*, b. p. 131°/15 mm., m. p. 43·5—44°, gave *ethyl* p-*thioltoluate*, b. p. 150°/18 mm., D_{25}^{25} 1·0708. The meta-acid and thiol ester were not prepared. The three toluic acids were separately heated in sealed tubes with ethyl mercaptan at 200° for one, two, four, eight, and sixteen days, and in each case the percentage of acid esterified was determined and the velocity constants calculated, using the formula for a bimolecular reaction. Ethyl *o*- and *p*-thioltoluates were similarly heated with water, and the percentage of ester saponified and the velocity constant determined. The three acids show the same relations as to velocities and limits of esterification with ethyl mercaptan as they do with ethyl alcohol, the limits being, however, much lower with the mercaptans than with the alcohols. The limit of esterification is in each case independent of the proportions of acid and mercaptan used, the three acids reaching practically the same limits of esterification under the above treatment. W. G.

The Synthesis of Amino-acids. Allylhippuric Acid. S. L. P. SØRENSEN (*Compt. rend. Lab. Carlsberg*, 1916, **11**, 212—222).—A more detailed account of work already published (compare A., 1908, i, 981). W. G.

Formation and Properties of *β*-**Amino-ketones derived from Aromatic Imines.** CHARLES MAYER (*Bull. Soc. chim.*, 1916, [iv], **19**, 427—432. Compare A., 1904, i, 832; 1905, i, 214, 857).—Other ketones than methyl ketones can be condensed with mines to give *β*-amino-ketones. In this way, benzylidene-*m*- and *p*-toluidines have been condensed with certain ketones.

Benzylidene-*p*-toluidine when condensed with methyl ethyl ketone gives *β*-p-*toluidino*-*β*-*phenylethyl ethyl ketone*,

$$C_7H_7\cdot NH\cdot CHPh\cdot CH_2\cdot COEt,$$

m. p. 156°. When this is dissolved in concentrated sulphuric acid or glacial acetic acid, and the solution poured on ice, styryl

ethyl ketone is obtained. A similar decomposition is produced if the ketone is warmed with acetyl chloride, benzoyl chloride, or phenylcarbimide. β-m-*Toluidino-β-phenylethyl ethyl ketone*, m. p. 127°, when warmed with phenylhydrazine hydrochloride gives phenylbenzylidenehydrazine, methyl ethyl ketone, and *m*-toluidine hydrochloride. With methyl hexyl ketone, benzylidene-*p*-toluidine gives β-p-*toluidino-β-phenylethyl hexyl ketone*,

$$C_7H_7\cdot NH\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_{13},$$

colourless needles, m. p. 85°, which by the action of sulphuric acid or when warmed in alcoholic solution with a few drops of pyridine gives cinnamenyl hexyl ketone. β-m-*Toluidino-β-phenylethyl nonyl ketone*, $C_7H_7\cdot NH\cdot CHPh\cdot CH_2\cdot CO\cdot C_9H_{19}$, felted needles, m. p. 72°, is decomposed by sulphuric acid, giving cinnamenyl nonyl ketone.

o-Hydroxybenzylideneaniline condenses very slowly with methyl ethyl ketone, giving *β-anilino-β-*o*-hydroxyphenylethyl ethyl ketone*, $HO\cdot C_6H_4\cdot CH(NHPh)\cdot CH_2\cdot COEt$, m. p. 232°, which when boiled in benzene solution with a few drops of pyridine gives a *compound*, m. p. 184°. With concentrated sulphuric acid, the ketone gives a violet-coloured *compound*, m. p. 130° (decomp.). W. G.

Isomerisation, Polymerisation, and Formation of Additive Products of α-Pinene. H. J. PRINS (*Chem. Weekblad*, 1916, **13**, 1264—1276).—On warming a solution of lævorotatory α-pinene in glacial acetic acid at 60—70° with 5% of phosphoric acid (D 1·7), *l*-limonene is formed, with development of heat. Strong mineral acids, and aluminium, ferric, and zinc chlorides convert α-pinene into a product resembling colophony. α-Pinene combines with water, alcohol, and organic acids, forming alcoholic derivatives of the borneol or terpineol type. A. J. W.

Isomeric Sabinols. VINCENZO PAOLINI and GIOVANNI REBORA (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 377—381. Compare A. 1911, i, 730; 1912, i, 635).—Discordant values have been given by different investigators for the physical constants of sabinol, but no attempt seems to have been made to separate stereoisomeric modifications. The authors have prepared from savin oil a *hydrogen phthalate* of sabinol, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{15}$, which recrystallises in tufts of white, silky needles, m. p. 95°, $[\alpha]_D$ −14°63 (in methyl alcohol). Hydrolysis of this ester yields sabinol, b. p 208°, D^{15} 0·9518, n_D^{18} 1·4895, $[\alpha]_D$ +7°56′, and treatment of the sabinol with phthalic anhydride yields solely the hydrogen phthalate just described. These two compounds appear to be definite chemical individuals.

That savin oil contains no other isomeric sabinol has been shown in the following manner. The uncrystallisable syrup obtained after removal of the solvent from the mother liquors of the hydrogen phthalate was converted into the strychnine salt, which when crystallised several times and hydrolysed with cold, dilute hydrochloric acid, gave only the acid phthalate described above *Strychnine sabinol phthalate*, $C_{39}H_{40}O_6N_2$, crystallises in shining white needles, m. p. 200—201°. T. H. P.

Theory of Vegetable Tanning. HENRY RICHARDSON PROCTER and JOHN ARTHUR WILSON (T., 1916, **109**, 1327—1331).—A theoretical paper, the results being based on previously published work. It is shown that the combination of tannins and hide fibre, and the effect of acids and neutral salts in the tanning process, are explained by the existence of "membrane potentials," as described by Donnan (A., 1911, ii, 848). Equations are given with regard to the relation of the various concentrations involved, which equations should also be applicable to dyeing processes.

T. S. P.

Saponification of 2 : 5-Dimethylfuran-3 : 4-dicarboxylic Ester at 50°. G. KORSCHUN and A. GOUNDER (*Bull. Soc. chim.*, 1916, [iv], **19**, 426; *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 690—691).—A molecule of the ester was treated with four molecules of potassium hydroxide in dilute solution, the results indicating that the process is one of saponification of the acid ester of the dicarboxylic acid. W. G.

Preparation of 2 : 3-Diketodihydrothionaphthens. R. STOLLÉ (D.R.-P., 291759; addition to D.R.-P., 281046; from *J. Soc. Chem. Ind.*, 1916, **35**, 1213).—2 : 3-Diketodihydrothionaphthens, $C_6H_3R{<}{}^{CO}_{S}{>}CO$, are obtained by treating aromatic mercaptans with oxalyl chloride and subjecting the resulting chlorides, R·S–CO·COCl, to the action of condensing agents. *Methyl-2 : 3-diketodihydrothionaphthen*, glistening, yellowish-red leaflets, m. p. 144°, is obtained in this way from *p*-thiocresol. H. W.

(A) Cephaeline *iso*Butyl Ether and (B) Cephaeline Propyl Ether and Salts Thereof. J. W. MEADER (Brit. Pats. (A), 1915, 11717 and (B) 11719; from *J. Soc. Chem. Ind.*, 1916, **35**, 1271).—*Cephaeline* iso*butyl ether* is produced by treating cephaeline with an alkali metal and an *iso*butyl haloid, for example, from *iso*butyl bromide, cephaeline, and a solution of sodium ethoxide in absolute alcohol. It is a varnish-like substance, easily soluble in alcohol, ether, or chloroform. It forms a crystalline *hydrobromide*, white needles, and *hydrochloride*.

Cephaeline propyl ether is similarly prepared, and resembles the *iso*butyl compound. H. W.

Process of the Condensation of Pyrrole with Acetone. V. V. TSCHELINCEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 105—127. Compare A., 1915, i, 990).—The condensation of pyrrole with acetone, which has been studied by von Baeyer, Dennstedt, and others, is a complex process, and the authors have now studied it in various media with the object of obtaining the intermediate as well as the final products.

In acetone, this condensation yields about equal proportions of: (1) The crystalline compound, $C_{28}H_{36}N_4$, m. p. 290—292, obtained by von Baeyer (A., 1886, 1043) and by Dennstedt and Zimmermann (A., 1887, 598, 1052); after several crystallisations from

acetone and alcohol and from benzene, the compound melts at 296°. (2) An amorphous compound, $C_{28}H_{36}ON_4$, m. p. above 180° (decomp.), which has the normal molecular weight in freezing benzene, but could not be obtained crystalline; when its solution is left in contact with the air, it undergoes gradual transformation into a compound which begins to decompose at about 230°, and gives analytical results in approximate correspondence with the ratios $C_{28}:H_{34}:O_6:N_4$, but was not obtained pure.

In alcohol, the condensation yields, in the cold, both the above products, but, in the hot, almost exclusively the crystalline compound (1).

In an aqueous medium containing a little hydrochloric acid and just sufficient acetone to dissolve the pyrrole used, the condensation gives, at the ordinary temperature, only a very small proportion of the crystalline compound, m. p. 290—292°, the preponderating product being the *compound*, $C_{25}H_{32}N_4$, which forms a solid, non-crystalline mass, has the normal molecular weight in freezing benzene, and is formed according to the equation

$$4C_4H_5N + 3COMe_2 = C_{25}H_{32}N_4 + 3H_2O.$$

Oxidation of this compound by means of the air yields: (1) a pink, powdery compound, $C_{28}H_{36}ON_4$, m. p. 152—154°, having the normal molecular weight in freezing bromoform; (2) a bright orange, amorphous, flocculent compound, $C_{28}H_{36}O_3N_4$, which begins to melt at about 92—95°, then decomposes without completely melting, and gives off gas at 115°; its cryoscopic behaviour in bromoform is normal; (3) an amorphous *compound*, $C_{28}H_{34}O_6N_4$ (?), which begins to decompose at 230°. The compound, $C_{25}H_{32}N_4$, is converted almost quantitatively into the crystalline compound, m. p. 290—292°, when heated with hydrochloric acid in presence of acetone.

The condensation of pyrrole with acetone takes place also in presence of nitric or sulphuric acid or sulphur dioxide, and, although far more slowly, in that of hydrogen sulphide; potassium hydroxide is without influence in this direction. The ordinary organic acids also bring about the condensation, which in this case yields: (1) the crystalline compound, m. p. 290—292°, and (2) a *compound*, $(C_{28}H_{36}ON_4)_3$, which forms small, pink crystals, beginning to decompose at 160°, and in freezing bromoform has the molecular weight corresponding with the trebled formula; when boiled with hydrochloric acid, this compound undergoes resinification and conversion into the crystalline product, m. p. 290—292°.

The latter compound and that now obtained by the authors, $C_{28}H_{32}N_4$, are of the same order of complexity as the natural pyrrole pigments, chlorophyll and hæmin, each of these consisting of four pyrrole nuclei. That not more than four nuclei are concerned in these condensations under both natural and artificial conditions is regarded as the result of stereochemical relations.

T. H. P.

Structure of the Condensation Products of Pyrrole and Acetone. V. V. Tschelincev and B. V. Tronov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 127—155. Compare preceding abstract).—To the two condensation products already described are given the names: $C_{25}H_{32}N_4$, "tetrapyrrole-triacetone condensation product," and $C_{28}H_{36}N_4$, "tetrapyrrole-tetra-acetone condensation product." The former is converted almost quantitatively into the latter when heated with acetone in presence of hydrochloric acid. The close relation of these two condensation products to etioporphyrin is shown by the fact that, on oxidation, they yield maleimide, whereas etioporphyrin gives a substituted maleimide.

The conclusions which have been drawn concerning the molecular configuration of these condensation products are based principally on their behaviour when distilled in the dry state and when treated with sodium alkyloxide. Recent work on pyrrole has, however, indicated that such conclusions are unwarranted, since, at a high temperature, complex molecular decompositions and reconstructions are known to occur, and the action of sodium alkyloxide takes place as well at the linkings between the pyrrole nuclei as at the free 2- and 3-positions of these nuclei. The question of the structures of these condensation products remains therefore open, and the following experiments have been made with a view to its elucidation.

When treated with magnesium propyl iodide, these condensation products (1 mol.) yield respectively 3·94 and 4·12 mols. of gas, so that it may be assumed with safety that, in each case, the four imino-groups of the pyrrole residues remain unchanged. Further, in ethereal solution, the organo-magnesium compounds formed with magnesium propyl iodide absorb carbon dioxide, giving products which, when decomposed, yield the absorbed carbon dioxide and the unchanged original compounds. This behaviour is as would be expected of compounds of the carbamic acid type, and confirms the fact that the magnesium residue replaces the iminic hydrogen.

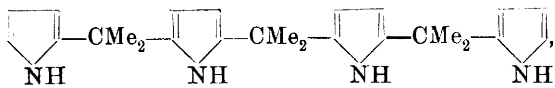
Dennstedt's statement that 1-substituted derivatives of pyrrole do not undergo condensation with acetone may possibly be true in some instances, but is not of general application. With 1-methylpyrrole, indeed, acetone condenses with moderate readiness, although not so energetically as with pyrrole itself. The *compound* obtained, $(C_{32}H_{42}N_4)_3$, forms crystals, m. p. 153—155°, and in freezing benzene has the molecular weight corresponding with the trebled formula. That the imino-group does not participate in the condensation with acetone is therefore confirmed.

When oxidised in acetic acid solution by means of chromic acid, both the tetrapyrrole-triacetone and the tetrapyrrole-tetra-acetone condensation products yield unsubstituted maleimide. It is evident, therefore, that the condensation does not involve removal of the hydrogen atom in the 3- or 4-position of the pyrrole nucleus.

The conclusion is drawn that the union of the pyrrole with the acetone in these condensation products takes place solely at the

2-positions of the nuclei. From the fact that dry distillation of the tetrapyrrole-tetra-acetone product yields a decomposition product with condensed acetone molecules indicates the possibility of the existence of the acetone in a condensed form in the condensation products. Experiment shows that the condensation of mesityl oxide and pyrrole in alcoholic solution in presence of hydrochloric acid yields a *compound*, $C_{32}H_{42}O_2N_4$ (?), m. p. about 170° (decomp.), quite different in type from those given by acetone and pyrrole under similar conditions.

These considerations lead to the formula



for the tetrapyrrole-triacetone condensation product, and in the tetrapyrrole-tetra-acetone product the free hydrogen atoms of the two CH-groups in the 2-positions of the terminal pyrrole nuclei are eliminated, and the corresponding carbon atoms united by way of a CMe_2-group. The probable accuracy of this relation between the two compounds is shown by the fact that the more complex is obtained in 90% yield when the simpler one is heated for five minutes on a water-bath in alcoholic solution with acetone and a little hydrochloric acid.

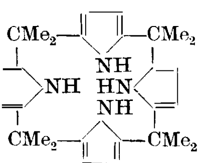
Towards hydroxylamine (compare Ciamician and Zanetti, A., 1890, 264, 1155; 1891, 1502; Fischer and Zimmermann, A., 1914, i, 318), the two condensation products exhibit widely varying behaviour. Even on prolonged boiling no action takes place with the tetra-acetone compound, but the tetrapyrrole-tetra-acetone condensation product readily yields a *compound*, $C_{38}H_{50}O_5N_4$ (?), which forms an amorphous, brownish-yellow powder, and undergoes oxidation with such facility that its accurate investigation is impossible. Fischer and Zimmermann (*loc. cit.*) studied the action of hydroxylamine on bilirubin, hæmin, porphyrinogen, etc., and obtained similarly unsatisfactory results.

Each of the two condensation products was treated with magnesium ethyl bromide, and the resultant products then subjected to the action of acetic anhydride. Under this treatment, the tetrapyrrole-tetra-acetone condensation product gave a very small proportion of a bright red compound, the bulk of the original substance remaining unchanged. The tetrapyrrole-triacetone condensation product gave, however, a good yield of a bright red, amorphous *compound*, $C_{45}H_{60}O_5N_4$ (?), whereas simple acetylation at the imino-groups should give a compound of the formula $C_{33}H_{40}O_4N_4$. The slight reactivity of the tetrapyrrole-tetra-acetone compound is regarded as due to its cyclic structure and to the absence of the highly active 2-hydrogen atoms of the pyrrole nucleus.

The action of hydriodic acid on chlorophyll or hæmin yields hæmopyrrole, the links connecting the pyrrole nuclei being broken, with formation of this very simple pyrrole derivative. Fischer and Bartholomäus (A., 1913, i, 209), who applied this action to definite

condensation products of pyrrole compounds with aldehydes and ketones, found that compounds of this type with side-chains in the 2-position, such as hæmin, break down in about two hours, whereas those with side-chains in the 3-position require for their resolution fourteen to sixteen hours at the boiling point. When a solution of the tetrapyrrole-triacetone condensation product in concentrated acetic acid is heated with hydriodic acid, or a solution of the tetrapyrrole-tetra-acetone product in a mixture of benzene and alcohol with hydrochloric acid, for one and a-half hours on a water-bath, a large proportion of an oily, resinous product, giving a green coloration with alkali hydroxide, is formed in either case. If, however, the period of heating is restricted to four to five minutes, in the first instance 44%, and in the second instance 45%, of the condensation product taken is converted into the other; the former transformation also takes place, although far more slowly, if the hydriodic acid is replaced by acetic acid. These results support the conclusion that the dimethylmethylene chains of these compounds are linked to the 2-positions of the pyrrole nuclei.

For the tetrapyrrole-tetra-acetone condensation product, a structure of the type of the annexed formula is proposed, this being analogous to Küster's formula for hæmin. Willstätter's objection to the latter on the ground that it contains a 16-membered ring, is discussed, and it is shown that the value of the "tension" in the closed ring of the authors' formula just given is small under any supposition, and, according to one arrangement, zero. T. H. P.



Saponification of some Pyrrolemonocarboxylic and Pyrroledicarboxylic Esters at a Temperature of 98·3—98·7°. G. Korschun and A. Gounder (*Bull. Soc. chim.*, 1916, [iv], **19**, 407—426; *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 667—690).—These measurements made at the higher temperature confirm the results already obtained at 50°, and, to a certain extent, some of the conclusions previously drawn (compare A., 1916, ii, 525). W. G.

Preparation of Vinyldiacetoneamine [2 : 2 : 6-Trimethyl-4-piperidone] and its Salts. A. T. King, F. A. Mason, and S. B. Schryver (Brit. Pat., 101738; from *J. Soc. Chem. Ind.*, 1916, **35**, 1235).—The action of an acetai of the type $CH_3{\cdot}CH(OR)_2$ with diacetoneamine or its salts, or with acetone saturated with ammonia, produces 2 : 2 : 6-trimethyl-4-piperidone or its salts according to the equation $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2 + CH_3{\cdot}CH(OR)_2 = \begin{array}{l}CH_2{\cdot}CO{\cdot}CH_2\\ MeCH{\cdot}NH{\cdot}CMe_2\end{array} + 2ROH$. Better yields (about 90% of the theoretical) are obtained in much shorter times than by previously published methods. Thus, the oxalate is obtained by heating

diacetoneamine hydrogen oxalate with diethylacetal in solution in normal butyl alcohol for three hours or in ethyl alcohol for seven hours. H. W.

Combination of Organic Acids [Salicylic Acid and 2-Phenylquinoline-4-carboxylic Acid]. ELI LILLY & Co. (U.S. Pat., 1916, 1203499, and Brit. Pat., 1916, 102136; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272).—A compound of salicylic acid and 2-phenylquinoline-4-carboxylic acid is produced by precipitating an equimolecular mixture of their alkali salts with a mineral acid. H. W.

Combination of Organic Acids [Ester of 2-Phenylquinoline-4-carboxylic Acid and Salicylic Acid]. ELI LILLY & Co. (U.S. Pat., 1203500; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272. Compare preceding abstract).—An ester of salicylic acid and 2-phenylquinoline-4-carboxylic acid, $C_9H_5NPh\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, is prepared by treating 2-phenylquinoline-4-carboxylic acid with thionyl chloride and combining the resulting chloride with salicylic acid. H. W.

2-Naphthylquinoline-4-carboxylic Acids. CHEM. FABRIK AUF AKTIEN VORM. E. SCHERING (U.S. Pat., 1197462; from *J. Soc. Chem. Ind.*, 1916, **35**, 1272).—2-Naphthylquinoline-4-carboxylic acids are prepared by condensing isatin with naphthyl methyl ketone in alkaline solution, or by condensing aniline with pyruvic acid and naphthaldehyde. For example, a solution of isatin (180 parts) in alcohol (500 parts) and potassium hydroxide solution (33%, 300 parts) is heated with α-naphthyl methyl ketone (90 parts) on the water-bath for some hours. After removal of alcohol, the product is precipitated by hydrochloric acid, redissolved in sodium carbonate solution, again precipitated, and crystallised from dilute alcohol. *2-α-Naphthylquinoline-4-carboxylic acid* forms yellowish-red needles, m. p. 198°; *2-β-naphthylquinoline-4-carboxylic acid*, yellow crystals, has m. p. 234°. Both acids are remedies for gout and rheumatism. H. W.

Action of the Grignard Reagent on Cyanogen Compounds. Synthesis of Amidines from Cyanamides. ROGER ADAMS and C. H. BEEBE (*J. Amer. Chem. Soc.*, 1916, **38**, 2768—2772).—Dibenzylcyanamide, when acted on with magnesium alkyl and aryl haloids, gives additive compounds which on decomposition yield the salts of substituted amidines. These salts are not easy to purify, owing to their solubility and their tendency to become coloured during crystallisation, it being necessary in one case to prepare the carbamide by the action of phenylcarbimide on the free amidine. The amidines themselves are mostly oils or very soluble solids with low melting points. The following compounds were prepared.

Dibenzylpropenylamidine hydrochloride,

$$N(CH_2Ph)_2\cdot CEt\colon NH,HCl,$$

rhombohedra, m. p. 204—204·5°.

Dibenzylbenzamidine hydrochloride,

$$N(CH_2Ph)_2\cdot CPh\colon NH,HCl,$$

rhombohedra, m. p. 211·5°. *Dibenzylbenzamidine* is a white solid, m. p. 70—71°.

Dibenzyl-p-*tolenylamidine hydrochloride*,

$$N(CH_2Ph)_2\cdot C(C_6H_4Me)\colon NH,HCl,$$

always contained a certain amount of a yellow impurity, but yielded *dibenzyl*-p-*tolenylamidinephenylcarbamate*,

$$N(CH_2Ph)_2\cdot C(C_6H_4Me)\colon N\cdot CO\cdot NHPh,$$

slender, white needles, m. p. 158°. W. G.

The Molecular Rearrangement of Triarylmethylazides. JAMES KUHN SENIOR (*J. Amer. Chem. Soc.*, 1916, **38**, 2718—2726).—Triphenylmethylazide, when heated in a sealed tube at 225° for one hour, undergoes molecular rearrangement, giving phenyliminobenzophenone, $CPh_3\cdot N_3 \longrightarrow CPh_3\cdot N + N_2 \longrightarrow CPh_2\colon N\cdot Ph + N_2$.

When *p*-chlorotriphenylmethyl chloride (compare Gomberg, A., 1904, i, 658, 988) is boiled with hydrazine hydrate in absolute ether, the main product is either p-*chlorotriphenylmethylhydrazine hydrochloride*, m. p. 122°, or *bis*-p-*chlorotriphenylmethylhydrazine*, m. p. 201°, according to the proportions of the reagent used. When this hydrazine hydrochloride is boiled in alcoholic solution with 7% hydrochloric acid, p-*chlorotriphenylmethylazide* is obtained as a gum, which when heated at 215° undergoes rearrangement, giving phenyliminochlorobenzophenone and chlorophenyliminobenzophenone in the molecular proportion of 68·1 to 31·9, these figures being in close agreement with those obtained by Leech for *p*-chlorotriphenylmethylhydroxylamine (compare A., 1914, i, 268). W. G.

The Molecular Rearrangement of *sym*-Bistriarylmethylhydrazines. JULIUS STIEGLITZ and JAMES KUHN SENIOR (*J. Amer. Chem. Soc.*, 1916, **38**, 2727—2736. Compare preceding abstract).—All attempts to cause a rearrangement of hydrazines by the loss of ammonia through treatment with concentrated acids or zinc chloride were unsuccessful. Attempts were then made to cause a rearrangement of *sym*-bistriarylmethylhydrazines, and these were successful, the hydrazines being heated with zinc chloride at 300° for ten minutes. Under these conditions, bistriphenylmethylhydrazine, $CPh_3\cdot NH\cdot NH\cdot CPh_3$, gave aniline and triphenylmethane, the formation of aniline being due to migration of a phenyl group from carbon to nitrogen. Bis-*p*-chlorotriphenylmethylhydrazine undergoes the same rearrangement, giving aniline and, in all probability, *p*-chloroaniline. The mechanism of the action is not yet clear, as it does not proceed smoothly. A number of attempts were made to rearrange unsymmetrical hydrazines and hydrazones, but they were all unsuccessful. W. G.

Preparation of Collargol. A. F. Gerasimov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 87—90, 251—253).—Investigations on the preparation of collargol by Paal's method (A., 1902, i, 653; ii, 500) show that the reduction to metallic silver takes place mainly, if not entirely, at the expense of the silver oxide, preparations with approximately the same proportion of silver being obtained with widely varying concentrations of silver nitrate. The percentage of silver in the preparations is increased but slightly by precipitation with acids.

On the basis of these results, the following method of obtaining collargol is recommended. The reducing mixture is prepared by shaking 100 grams of albumin with a solution of 15 grams of sodium hydroxide in 500 c.c. of water until it is uniformly distributed throughout the liquid, which is then heated for about an hour on a water-bath and freed from a little flocculent precipitate by filtration. To 27—30 grams of this solution is added the silver oxide obtained by precipitating a solution of 10 grams of silver nitrate with potassium hydroxide and washing five times by decantation. The mixture is diluted to about 200 c.c. and heated on a water-bath, with constant shaking, for forty to sixty minutes. When cold, the liquid is precipitated with a few drops of concentrated acetic acid, and the precipitate washed five or six times and dissolved in water in presence of a minimal quantity of sodium hydroxide. The liquid is allowed to settle, and dried either in a desiccator over sulphuric acid or in a vacuum at about 40°, or in a current of air free from dust; over-drying should, however, be avoided. In this way, a blue powder containing about 75% of silver is obtained. T. H. P.

Protein Copper Compounds. Thomas B. Osborne and Charles S. Leavenworth (*J. Biol. Chem.*, 1916, **28**, 109—123).—On adding copper sulphate solution to an alkaline solution of edestin or gliadin, a blue copper protein compound is precipitated of variable composition, which is insoluble in excess of the copper sulphate. When kept, the colour of the precipitate changes to brown, due to decomposition, with liberation of partly dehydrated copper hydroxide. The authors suggest that the copper unites with the imino-nitrogen of the R·CO·NH·R groups. H. W. B.

Antigenic Properties of β-Nucleoproteins. H. Gideon Wells (*J. Biol. Chem.*, 1916, **28**, 11—16).—The nucleoproteins extracted from tissues by cold water, dilute salt, or weak alkaline solutions lose their antigenic properties on being heated at 100°. The so-called β-nucleoproteins, however, which are obtained from various tissues by extracting with boiling water, possess definite antigenic properties demonstrable by the anaphylactic reaction. Judging from the degree of anaphylaxis produced, the β-nucleoproteins from the pancreas and spleen of the ox and from the pancreas of the pig, seem to be similar, but not identical.

H. W. B.

Rotatory Power of Nucleic Acids and of Nucleates of the Alkali Metals. M. A. RAKUZIN and (MLLE.) EK. MAKS. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 97—99. Compare Rakuzin and Logunova, A., 1915, i, 1017).—Measurement of the rotation of Parke, Davis, & Co.'s 5% nucleic acid solution gives the value $[\alpha]_D$ +68·51° for the specific rotation of the nucleic acid. Dilute nucleic acid solutions were neutralised towards phenolphthalein by means of decinormal alkali hydroxide solutions, and the rotatory powers of the alkali nucleates thus obtained then measured, the values of $[\alpha]_D$ being: lithium salt, +21·73°; ammonium, +24·77°; sodium, +29·58°; and potassium, +35·39°. Thus, just as with the caseinogenates, the specific rotation of the alkali nucleates increases with the atomic weight of the metal. The rotations of the nucleates are, however, less than that of the nucleic acid, whereas caseinogenates give higher rotations than caseinogen. T. H. P.

The Significance of Electrolytes in Processes of Imbibition. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1916, **77**, 329—332).—The differences between the results obtained by the author and those of Lenk (A., 1916, i, 346) on the influence of salts on the imbibition of water by gelatin are due to the fact that the author worked with nearly dry plates of the material, whereas Lenk worked with plates which had already imbibed 80—85% of water. The latter was therefore only investigating the action of salts on an intermediate stage of the imbibition process, whereas the author had ascertained their action on the final equilibrium and on the whole course of the imbibition. S. B. S.

Influence of Acetic Acid on the Synthesising and Hydrolysing Properties of β-Glucosidase. EM. BOURQUELOT and A. AUBRY (*J. Pharm. Chim.*, 1916, [vii], **14**, 359—363. Compare A., 1915, i, 604).—β-Glucosidase is more resistant to the injurious action of acetic acid than is α-glucosidase, synthesis taking place almost normally up to a content of 0·1% of acetic acid. Higher concentrations of acetic acid retard the synthesis, owing to the progressive destruction of the enzyme. Similar results were obtained in studying the hydrolysing action of the enzyme in the presence of acetic acid. W. G.

Physiological Chemistry.

Relation between the Water and the Dextrose Concentration of the Blood. ALMA HILLER and HERMAN O. MOSENTHAL (*J. Biol. Chem.*, 1916, **28**, 197—202).—In normal individuals, the blood contains about 78·5% of water. There may be a variation of about 1% of this concentration during the course of a few minutes

without any apparent cause. In those conditions, pathological or experimental, in which the amount of dextrose in the blood is diminished or increased, there is no corresponding change in the concentration of the water in the blood. In diabetes, for instance, the water content of the blood is normal, notwithstanding the hyperglycæmia and polyuria which may be present. H. W. B.

Changes in the Urea Content of Blood and Tissues of Guinea-pigs Maintained on an Exclusive Oat Diet. HOWARD B. LEWIS and WALTER G. KARR (*J. Biol. Chem.*, 1916, **28**, 17—25. Compare Funk, A., 1916, i, 696).—The appearance of scorbutic symptoms in guinea-pigs fed on an exclusive oat diet is accompanied by a large increase in the amount of urea in the blood and tissues. The addition of cabbage or orange juice to the diet prevents the disease, and simultaneously prevents the rise in the urea content of the blood and tissues of the animal. Sodium citrate cannot replace the cabbage or orange juice, so that the pathological condition cannot be due to the production of acidosis. A satisfactory explanation of the connexion between the scorbutic condition and the high urea figures is not given by the authors.
H. W. B.

Enzymes in Blood. G. SATTA (*Arch. ital. de Biol.*, 1915, **64**, 118—122; from *Physiol. Abstr.*, 1916, **1**, 296).—If the serum proteins are fractionated (the globulin being precipitated by carbon dioxide or salted out with sodium chloride), the following enzymes, tributyrase, amylase, and glycyl-*l*-tyrosinase, are contained in the albumin fraction. G. B.

The Coagulation of the Blood. I. B. STUBER and R. HEIM (*Biochem. Zeitsch.*, 1916, **77**, 333—357).—Coagulation of plasma can be caused by the addition of glycerides, and the fatty acids have a specific action in causing this phenomenon. The coagulating action of the acid increases with increase in the number of carbon atoms in the acid, and acids such as palmitic and stearic acids exert therefore a greater coagulating action than the lower acids in the series. It is important, however, that an excess of acid is not added, as this inhibits the coagulation. The authors draw the conclusion that the optimal conditions for coagulation lie in the neighbourhood of the isoelectric point. The fats and fatty acids were added in the form of emulsions. It is conceivable that the coagulum is a complex of fibrin with a fatty acid, but this point is not definitely decided. S. B. S.

The Coagulation of the Blood. II. B. STUBER and R. HEIM (*Biochem. Zeitsch.*, 1916, **77**, 358—374).—The action of ferments on the coagulation process was investigated, and it was found that those produce the greatest coagulative effect which possess the greatest lipoclastic activity, and there is a proportionality between this factor and the capacity for accelerating coagulation. The activity of the thrombokinase of Morawitz is due chiefly to the

substances contained therein which are soluble in ether, but the lipase of the liver is also a coagulating factor. The coagulative action of extracts of organs appears to be due to the fact that they contain fats and a lipase. S. B. S.

The Coagulation of the Blood. III. B. STUBER and FR. PARTSCH (*Biochem. Zeitsch.*, 1916, **77**, 375—387).—The results of Bordet and Delange and of Zack are confirmed, according to which plasma which has been deprived of its lipoid substances by extraction with ether and other organic solvents loses its capacity for coagulation. The fact is also confirmed that the coagulative power is restored by the addition of lipoids. This restorative action is not, as has been thought by other authors, a specific action of lecithin, but is the action of fats generally in the presence of a lipase. The results confirm the general conception of the authors as to the part played by fats and lipase in the coagulative process. S. B. S.

Fibrin and its Relationship to Problems of Biology and Colloidal Chemistry; the Problem of Blood Coagulation. X. The Micellar Crystalline Character of Fibrin. E. HEKMA (*Biochem. Zeitsch.*, 1916, **77**, 273—282).—A general account is given of the conversion of the fibrin sols into gels and fibre, and the application of von Nägeli's micellar theory to these changes is discussed. S. B. S.

Structure of the Fibrin-gel and Theories of Gel-formation. W. H. HOWELL (*Amer. J. Physiol.*, 1916, **40**, 526—553; from *Physiol. Abstr.*, 1916, **1**, 223).—In the clotting of vertebrate blood, as observed under the ultramicroscope, the fibrin is first deposited as needles formed by an aggregation of fibrinogen particles. Vectorial forces, like those involved in crystallisation, are brought into play. The needles form a close meshwork and appear to become adherent. Under certain conditions, such as increased alkalinity, the gel may be devoid of this crystalline character and be formed by amorphous aggregation. The fibrin gel is clearly a heterogeneous system of a continuous, more liquid phase between trabeculæ composed of crystalline needles and constituting the more solid phase. The structure is reticular or sponge-like, and not a honeycomb.

Fibrinogen may have either a positive or negative electrical charge, according to the reaction of the medium. The behaviour towards thrombin differs in the two cases, the vectorial characteristic being connected with the positive charge, or adsorption of hydrogen ions.

Since the gel has not a honeycomb structure, the retention of water and maintenance of shape, as if possessing solid properties, cannot be due to the merely mechanical enclosure of water in cells. It is suggested that the water is held at the surface of the solid phase by molecular forces, such as those responsible for adsorption. G. B.

Metabolism of Dextrose in Surviving Organs. I. Action of Intestinal Tissue on Dextrose Circulating therein. U. LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 390—395).—When Tyrode's solution containing dextrose is circulated in the intestinal segment of a dog, the proportion of dextrose in the circulating liquid undergoes marked diminution, which in some cases amounts to 50%. At the same time, the carbohydrate-content of the intestine shows an increase, but this is never more than sufficient to account for the disappearance of 30—35% of the dextrose. When defibrinated blood containing dextrose is similarly circulated, the diminution in the reducing power of the circulating liquid is even greater than when Tyrode's solution is used; in this case, the carbohydrate-content of the intestine also diminishes considerably, marked consumption of the pre-existent dextrose thus taking place.

Similar differences were observed with amino-acids circulating in surviving organs in solution in blood and in Ringer's solution, but in the present case the phenomenon is particularly marked, the volume of liquid traversing the intestine per unit of time being appreciably less when blood is used than with the artificial liquid. The results show, indeed, that the more closely the conditions of the artificial circulation approximate to those of the organ *in vivo*, the less is the quantity of dextrose accumulating in the intestine and the greater the tendency of the organ to destroy the dextrose circulating in it. T. H. P.

Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells. IV. Ratio of the Concentration required for the Accelerating and Antagonistic Action on the Diffusion of Potassium Salts. JACQUES LOEB (*J. Biol. Chem.*, 1916, **28**, 175—184. Compare this vol., i, 67).—The addition of a second salt to a $M/8$-potassium chloride solution has the four following effects on *Fundulus* eggs according to the concentration: (1) Beginning with the lowest concentration of the second salt, the addition has often a slightly retarding effect on the diffusion of potassium chloride through the membrane into the egg; (2) with a further increase of the concentration of the second salt ($M/4$-sodium chloride or $M/512$-sodium citrate), an acceleration of the diffusion is noticeable (general salt effect); (3) with a still further increase of the concentration ($M/2$- to M-sodium chloride or $M/256$- to $M/128$-sodium citrate), a retardation of the diffusion occurs (antagonistic salt effect); (4) with a still higher concentration the eggs are killed more rapidly, probably not through the diffusion of the potassium chloride, but of the second salt into the egg. The ratio of the antagonistic to the accelerating concentration was found to be about 2:1 for different sodium salts. H. W. B.

Chinese Preserved Eggs. Pidan. KATHARINE BLUNT and CHI CHE WANG (*J. Biol. Chem.*, 1916, **28**, 125—134).—Pidan is prepared by preserving ducks' eggs in a mixture of an infusion

of black tea, lime, salt, and wood ashes. After five months, the eggs are coated with rice hulls, and are then ready for eating.

The results of the analysis of pidan show that the following changes take place during its formation from fresh ducks' eggs: Water is transferred from the white to the yolk; alkali salts are absorbed from the preserving mixture; the lecithin and total ethereal extract diminish in quantity; and the ammonia nitrogen, amino-nitrogen, and total non-coagulable nitrogen increase very greatly. It is therefore evident that the production of pidan from fresh eggs is due to the combined action of alkali, bacteria, and enzymes on the proteins and phospho-lipoids in the eggs.

H. W. B.

Method for the Measurement of the Urea-excreting Function of the Kidneys. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1916, **28**, 251—259).—The new method is based on the results of some experiments on rabbits. Urine and blood are collected simultaneously, and the ratio—urea in grams in one hour's urine to urea in grams in 100 c.c. of blood—determined before and after the ligature of one ureter, whilst the animals are taking similar food and the same amount of water. In most cases the ratio remains constant, because the single kidney remaining after the operation is sufficient to meet ordinary demands. If, however, urea is injected, additional strain is thrown on the kidneys, and the ratio after the operation is invariably lower than it is before the operation. The authors propose to employ the method for the early detection of pathological conditions arising from defective kidney function, such as Bright's disease. H. W. B.

New Constituents of Milk. II. The Distribution of Phosphatides in Milk. THOMAS B. OSBORNE and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1916, **28**, 1—9. Compare A., 1915, i, 920).—By operating with very large quantities of milk, the authors are able to show that phosphatides can be extracted from the caseinogen precipitated by the addition of dilute hydrochloric acid to milk, as well as from the "lactalbumin" coagulum obtained by heating the filtrate from the caseinogen. The precipitate produced by treating skimmed milk, free from caseïnogen and lactalbumin, with sodium hydroxide until neutral to phenolphthalein also contains a small amount of phosphatides, together with protein. The filtrate containing the non-protein constituents of milk contains at the most only minute traces of phosphatides.

A litre of milk contains about 27 milligrams of phosphatides which are intimately associated with the protein constituents of milk, and possibly combined with them as "lecithalbumins."

H. W. B.

Urinary and Fæcal Output of Calcium in Normal Men, together with Observations on the Hydrogen-Ion Concentration of Urine and Fæces. C. FERDINAND NELSON and J. L. WILLIAMS (*J. Biol. Chem.*, 1916, **28**, 231—236).—The authors have

measured the daily urinary and fæcal output of calcium, calculated as oxide, over periods of 5 days for five apparently normal individuals of ages ranging from thirteen to seventy years. The urinary excretion varies from 0·1754 to 0·6186 gram, the fæcal excretion from 0·4125 to 0·8010 gram, and the total daily excretion from 0·5879 to 1·4196 gram of calcium oxide. All the subjects studied were on ordinary mixed diets. The authors do not draw any conclusions regarding the relation between the observed hydrogen-ion concentration of the urine and the corresponding output of calcium. H. W. B.

Calcium and Magnesium Content of Normal Urine. C. FERDINAND NELSON and W. E. BURNS (*J. Biol. Chem.*, 1916, **28**, 237—240).—The daily urinary output of calcium and magnesium has been estimated in the cases of twenty-five healthy individuals. In the majority of cases, the output of calcium exceeds that of magnesium. Apparently whichever element predominates does so constantly, or nearly so, and this phenomenon seems to be independent of the character of the food ingested. H. W. B.

Influence of Sodium Carbonate, Administered by Duodenal Tube, on Human Diabetes. J. R. MURLIN and L. F. CRAVER, with WALTER L. NILES and WARREN COLEMAN (*J. Biol. Chem.*, 1916, **28**, 289—314).—Six cases of diabetes are described in which solutions of sodium carbonate or sodium hydrogen carbonate are introduced directly into the duodenum by means of an Einhorn's duodenal tube. In each case, the effects are a reduction of the glycosuria and hyperglycæmia. When the administration of alkali is discontinued, the dextrose in the blood and urine slowly returns to its original level. H. W. B.

Pancreatic Diabetes in the Dog. IV. Influence of Pylorus Exclusion and of Gastrectomy on the Effects of Pancreatectomy. J. R. MURLIN and J. E. SWEET (*J. Biol. Chem.*, 1916, **28**, 261—288).—The authors believe that in pancreatic diabetes the hydrochloric acid produced in the stomach and left unneutralised in the duodenum is absorbed by the portal system and carried to the liver, where it exerts its toxic action (compare Murlin and Kramer, this vol., i, 69). If the acid is excluded from the duodenum by ligaturing the pylorus or by excision of the stomach, the onset of pancreatic diabetes after pancreatectomy should therefore be prevented or delayed. These operations have been carried out on dogs, and it is found that in most cases little or no glycosuria follows the subsequent operation of pancreatectomy. In the case of one dog, however, which was fed after gastrectomy on peptonised food introduced directly into the duodenum, so that a considerable amount of glycogen was probably stored in the liver previous to pancreatectomy, a severe diabetes with marked hyperglycæmia followed the removal of the pancreas. In general, dogs with the pancreas removed after gastrectomy do not exhibit the usual profound toxæmia of a simple pancreatectomy.

The authors suggest that the pancreatic hormone produced by the islands of Langerhans may be an alkaline substance which maintains the proper concentration of hydrogen ion in the tissues for the biochemical oxidation of dextrose. The internal secretion thus resembles the external secretion which contains the alkali requisite for the neutralisation of the hydrochloric acid entering the duodenum from the stomach. H. W. B.

Composition, especially the Hydrogen-Ion Concentration, of Sea-water in Relation to Marine Organisms. J. F. McClendon (*J. Biol. Chem.*, 1916, **28**, 135—152).—The P_H of sea-water at Tortugas, Florida, from the surface to a depth of 35 metres varies from 8·1 to 8·22, which is about the average usually found for ocean water.

An artificial sea-water in which even the most delicate marine organisms can be kept alive for considerable periods may be prepared from the following normal solutions: 22 c.c. of $M/2$-calcium chloride, 50·21 c.c. of $M/2$-magnesium chloride, 57·09 c.c. of $M/2$-magnesium sulphate, 10·23 c.c. of M-potassium chloride, 483·65 c.c. of M-sodium chloride, 0·8 c.c. of M-sodium bromide, 2·32 c.c. of M-sodium hydrogen carbonate, and 373·63 c.c. of water. The mixture must be aerated until it has a P_H of about 8·15. H. W. B.

A New Group of Antagonising Atoms. II. T. P. Feenstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 341—344).—In a previous paper (*ibid.*, 1916, **19**, 99) it was shown that uranium can take the place of potassium in Locke-Ringer's solution, and that this substitution is not affected by the separation of the uranium from its products of transformation. Further experiments show that the potassium may also be replaced by thorium, but in this case it is not possible to say to what extent the action is due to radiothorium, since this cannot be separated from the thorium.

Both uranium and thorium are antagonistic to calcium in the same way as potassium and rubidium are, and the supposition that the antagonism is in some way connected with the valency of the ions does not appear to be consistent with the new observations.

H. M. D.

Elimination of Malates after Subcutaneous Injection of Sodium Malate. Louis Elsberg Wise (*J. Biol. Chem.*, 1916, **28**, 185—196).—Sodium malate may be injected subcutaneously into rabbits or cats in quantities up to 1 gram per kilo. without the occurrence of any toxic symptoms. Small amounts of the injected substance are recovered unchanged from the urine.

The method for the estimation of malic acid in urine described by Ohta (A., 1912, ii, 1076) affords satisfactory results if the urine is saturated by the addition of powdered uranyl acetate instead of being treated with a saturated solution of the reagent.

H. W. B.

Action of Sodium Citrate and its Decomposition in the Body. WILLIAM SALANT and LOUIS E. WISE (*J. Biol. Chem.*, 1916, **28**, 27—58).—The authors describe a method for the estimation of small amounts of citric acid in urine, based on Denigès's reaction. A modification of the method is employed for the approximate estimation of very small amounts of citrate in blood.

The ingestion of large quantities of sodium citrate by rabbits renders the urine alkaline. Only traces of citrate are found in these circumstances in the blood and urine, and toxic effects are not observed unless the amount of citrate ingested has been very large.

Sodium citrate disappears rapidly from the circulation after intravenous injection into rabbits, cats, and dogs; acute toxic symptoms are produced, the fatal dose varying from 0·4 to 1·6 grams per kilo. The urine remains free from citrate until the amount of citrate injected exceeds 0·5 gram per kilo.

The subcutaneous injection of sodium citrate may also occasion acute toxic symptoms. H. W. B.

Tolerance to Morphine. II. The Specificity of the Tolerance. JOHANNES BIBERFELD (*Biochem. Zeitsch.*, 1916, **77**, 283—297).—Dogs which have acquired tolerance to morphine by repeated injection of the drug do not acquire tolerance to scopolamine, cocaine, or even morphine derivatives, such as heroine (diacetylmorphine). The course of the acquisition to morphine is not influenced by feeding with cholesterol. After cessation for ten days of the injections, the cerebral reaction to morphine does not reappear, although the animal has not lost tolerance in some other respects. The immunising substances cannot always be detected when the serum of the immunised animals is transferred to other animals. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

General Conceptions of Intoxication. IV. The Nature of Substances which Accelerate the Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **77**, 402—404. Compare this vol., i, 71).—The substance in serum which promotes the capacity of bacteria for hydrolysing urea is soluble in water or alcohol, but insoluble in ether, light petroleum, or acetone.

S. B. S.

General Conceptions of Intoxication. V. The Stimulative Action of Dextrose on the Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **77**, 405—407).—Dextrose stimulates bacterial decomposition of urea. S. B. S.

Biochemical Changes in Protein Cleavage Products produced by Bacteria. II. TAKAOKI SASAKI (*Acta Scholae Med., Kyoto*, 1916, **1**, 103—113; from *Physiol. Abstr.*, 1916, **1**, 283).—*Bacillus proteus*, freshly isolated from putrid pancreas, destroys tyrosine and converts it largely into *d*-hydroxyphenyl-lactic acid and, to a smaller extent, into hydroxyphenylpropionic acid. *Bacillus subtilis*, in pure culture from straw infusion, produces, on the other hand, the antipodal *l*-hydroxyphenyllactic acid, together with other substances as yet unidentified. G. B.

Influence of Short, Slight Rises in Temperature on the Progress of Fermentation. CHARLES RICHET and HENRY CARDOT (*Compt. rend.*, 1916, **163**, 954—959).—If a liquid undergoing lactic fermentation is heated for five minutes at a temperature of 57—58°, the activity of the ferment is materially diminished. The effect is noticeable at the end of one minute, and increases considerably with the time. If the heating is repeated for further periods of five minutes, there is a further diminution in the acidity produced. Pathogenic organisms being much more susceptible to heat than the lactic ferment, the authors suggest the irrigation of wounds with water at 52—54° as a means of cleansing them.
W. G.

Action of Copper Sulphate on the Algæ of Potable Water. ATILIO A. BADO (*Pamphlet*, 1916, 15 pp.).—An account of the application of the copper sulphate method to the elimination of algæ from the water supply of Rio de la Plata. A. J. W.

Relationship existing between the Oxydase Activity of Plant Juices and their Hydrogen-Ion Concentrations. The Cause of Oxydase Activity in Plant Tissues. HERBERT H. BUNZELL (*J. Biol. Chem.*, 1916, **28**, 315—333).—The results indicate that the greatest oxydase activity occurs at or near the neutral point, and that acids inhibit the action of oxydases. The author suggests that oxydase activity is due to the presence of colloidal proteins, which through surface action are capable of condensing oxygen as well as oxidisable substances at their surfaces, resulting in the oxidation of those substances. The differences in oxydase activity of the various plant tissues are therefore due to the differing composition of their respective proteins. H. W. B.

Occurrence and Physiological Significance of Flavone Derivatives in Plants. K. SHIBATA, I. NAGAI, and M. KISHIDA (*J. Biol. Chem.*, 1916, **28**, 93—108).—The authors describe a new method for the detection of the presence of flavones in plant tissues. The tissue is extracted with hot alcohol, and a few c.c. of the extract are then heated with a drop of mercury the size of a pea, a small amount of magnesium powder, and a few drops of concentrated hydrochloric acid in a test-tube. In the presence of flavone derivatives, reduction takes place with a vigorous generation of hydrogen gas and the production of a red colour. The intensity of the colour produced is regarded as a measure of the amount of flavone present. By means of this test, the authors are

able to demonstrate the presence of flavone derivatives in almost all plants, including mosses, ferns, grasses, conifers, palms, and angiosperms.

The authors suggest that the flavone derivatives dissolved in the cell sap have to fulfil the important physiological function of absorbing the ultra-violet rays of the sunlight, by means of which the living protoplasm and its biochemical agencies are protected from the injurious action of the rays. In support of this theory, it is found that the flavone derivatives in plants are almost exclusively limited to the epidermis and the peripheral parenchymatous layer of the aerial parts. Further, plants growing in tropical or alpine regions are always rich in flavones, except those which are fully protected from the action of the excessive illumination by some means of a morphological or anatomical nature.

The green leaves of deciduous trees, which produce anthocyanin in autumn, contain a considerable quantity of flavone derivatives. The production of autumnal colour is due to the biochemical change resulting in the reduction of the already existing flavones in the leaf into anthocyanin. H. W. B.

Kafirin, an Alcohol-soluble Protein from Kafir, Andropogon sorghum. Carl O. Johns and J. F. Brewster (*J. Biol. Chem.*, 1916, **28**, 59—65).—The new protein, *kafirin*, constitutes more than one-half the total protein in kafir seeds. It contains C 55·19, H 7·36, O 20·41, N 16·44, and S 0·60%, and thus resembles zein. It differs from zein in containing lysine and tryptophan, and in requiring a larger proportion of 70% alcohol for its solution. The estimation of the diamino-acids by Van Slyke's method indicated the presence of 1·58% of arginine, 0·90% of lysine, and 1·0% of histidine in kafirin. H. W. B.

Chemical Investigation of Rain Water Collected at Various Sites in the [Sheffield] City Area. W. Palmer Wynne (Rep. to the Health Committee of the Sheffield City Council, 1914—15, 15 pp.).—A detailed account of the results obtained at Sheffield in connexion with the investigation of atmospheric pollution (A., 1916, i, 592).

With reference to the method employed, it is pointed out that the greatest pollution occurs on calm, foggy days without rain, and that the monthly analyses of the rain-water fail to give any record of the atmospheric impurities under these conditions. The conclusion is drawn that the total amounts of impurities, as indicated by the sums of the monthly results, represent minimum values at most.

In the Attercliffe area, the results do not show the progressive increase in contamination which would be expected from the increased industrial activity.

It is suggested that more useful results could be obtained by drawing air through water, continuously and at a given rate, so as to retain all the impurities. N. H. J. M.

Organic Chemistry

Relation between Filtration of the [Solid] Paraffins of Naphtha and their Adsorption. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 718—720).—By a single filtration of naphtha through kaolin, the lower fraction of the solid paraffins is adsorbed to the same extent as by adsorption in other ways; the adsorption is irreversible, and hot water extracts nothing from the separated adsorbent. T. H. P.

Irreversible Adsorption of the "Carbonaceous Substances" of Petroleum. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 720—724. Compare A., 1915, i, 489).—The adsorption of a 1% solution of petroleum in benzene by animal charcoal and by calcined kaolin has been investigated. The "carbonaceous substances," that is, those which cause polarimetric opacity, are adsorbed less rapidly by kaolin than by animal charcoal, but their adsorption is complete if the carbonisation constant (coefficient of polarimetric opacity) is not less than 18%. The adsorption is irreversible, neither boiling light petroleum nor boiling water extracting anything from the adsorbent after use. Other conclusions drawn from the results obtained are: (1) The qualitative and quantitative results of adsorption depend on the character and proportion of the adsorbent, but not on the mode of its application. (2) The velocity of adsorption is very high, since with a suitable concentration of the solution, filtration of the latter through a layer of adsorbent 2·5 cm. in thickness brings about adsorption. (3) The adsorbent used as filtering layer for petroleum may be regenerated by ignition.

The bearing of these results on the natural filtration–distillation processes of petroleum is discussed. T. H. P.

Pyrogenesis of Hydrocarbons. E. Lawson Lomax, A. E. Dunstan and F. B. Thole (*J. Inst. Petrol. Tech.*, 1916, **3**, 36—120).—A general account of the subject is given, together with chronological lists of the literature and patents. T. H. P.

Thermal and Pressure Decomposition of Pentanes and Hexanes. G. Egloff (*Met. Chem. Eng.*, 1916, **15**, 692—696; from *J. Soc. Chem. Ind.*, 1917, **36**, 76).—The mixture of pentanes and hexanes used was derived from light petroleum after removal of unsaturated hydrocarbons; it had $D^{15\cdot5}$ 0·656, and, on distillation, yielded: b. p. below 40°, 36·0%; b. p. 40—60°, 29·0%; b. p. 60—70°, 34·2%. It was subjected to temperatures of 450°, 500°, 650°, and 725°, and pressures of 1 and 12 atmospheres, and the recovered oil examined for benzene, toluene, xylene, naphthalene, and anthracene. The percentage yield of recovered oil decreased with increase of pressure and temperature, the maximum yield

being obtained at 450° and 1 atmosphere. At 650° and 12 atmospheres, and at 725° and 1 atmosphere, the original oil decomposed completely into carbon and gas. The percentage of benzene in the recovered oil increased as pressure and temperature were increased, the maximum of 15·1% being found at 650° and 1 atmosphere. The toluene and xylene content of the recovered oil decreased with increased temperature and pressure, the maximum being 6·9% for toluene and 8·2% for xylene, both at 450° and 1 atmosphere. Naphthalene and anthracene in the recovered oil increased with temperature and pressure, a maximum of 5·6% for naphthalene and 4·2% for anthracene being obtained at 650° and 1 atmosphere. The yields of benzene, toluene, and xylene, calculated on the basis of the original oil, decreased with increase of temperature and pressure; the highest yields were 3·2% for benzene, 5% for toluene, and 5·9% for xylene, all at 450° and 12 atmospheres. Naphthalene and anthracene increased with increasing temperature and decreased with increasing pressure; the maximum for naphthalene was 1·7% and for anthracene 1·2%, both at 500° and 1 atmosphere. The mechanism of the formation of aromatic hydrocarbons from pentanes and hexanes is probably represented by the following scheme: pentanes and hexanes $\longrightarrow$ $C_5H_{10}+CH_4 \longrightarrow C_2H_4+C_3H_6 \longrightarrow$ naphthenes $\longrightarrow$ aromatic hydrocarbons. H. W.

Effect of Temperature on the Formation of Benzene, Toluene, Xylene, Naphthalene, and Anthracene from Petroleum at Atmospheric Pressure. GUSTAV EGLOFF and THOMAS J. TWOMEY (*J. Physical Chem.*, 1916, **20**, 121—150).—A long historical review of the work done since the time of Faraday on the production of gas from various oils is given, and conclusions are drawn as to the relative amounts of the various constituents of the liquid products with variation of the conditions of the experiments. In the present series of experiments, weighed quantities of petroleum (574 grams) were passed through an electrically heated furnace at temperatures from 450° to 875°. The oil was fed into the furnace at a constant rate (246 grams per hour), and the amount of gas and liquid produced measured. The liquid was then distilled, and the fractions 170—230°, 230—270°, and 270° to tar collected. These were examined and their specific gravities recorded. The results of the experiments are given in numerous tables and curves. It is shown that the percentage of cracked oil obtained decreased slowly with increase of temperature from 450—550°; it decreased rapidly from 550° to 700°, and at a much slower rate from 700° to 875°. The formation of gas increased proportionally with change of temperature similarly to the percentage of the cracked oil. The density of the cracked oil increased with temperature. Temperatures of 450° to 600° produced in the cracked oil more toluene and xylene than benzene, and more toluene than xylene. No naphthalene or anthracene was formed at these temperatures. At 650° more toluene than benzene, and more benzene than xylene, were formed, but no naphthalene or

anthracene. Temperatures of 700° to 850° yielded uniformly more benzene than toluene or xylene, but more toluene than xylene. The formation of naphthalene began at 750°, and of anthracene at 800°, and both increased with the temperature. The formation of benzene in the cracked oil attained a maximum of 21% at 800°, of toluene 8·3% at 700°, and of xylene 7·2% at 700°. Beyond these respective temperatures, the formation of each decreased fairly rapidly with rise in temperature. The largest percentage of naphthalene obtained was 11·4 at 875°, and anthracene 2·5 at the same temperature. Temperatures 450° to 700° produced benzene, toluene, and xylene mixed with aliphatic compounds. The higher temperatures 750° to 875° yielded aromatic compounds practically free from aliphatic compounds. On the basis of the oil used, a maximum of 4·7% of benzene was obtained at 750°, 3·1% toluene at 650°, 1·9% xylene at 700°, 2·0% naphthalene at 800°, and 0·3% anthracene at 800°. The experimental evidence indicates that the formation of the individual aromatic compounds with change of temperature follows the scheme:

$$\begin{matrix}\text{Higher}\\ \text{homologues}\end{matrix} \longrightarrow \begin{Bmatrix}\text{Toluene}\\ \text{Xylene}\end{Bmatrix} \longrightarrow \text{Benzene} \longrightarrow \text{Naphthalene} \longrightarrow \text{Anthracene.}$$

J. F. S.

Refractometric Investigations of Hydrocarbons with Two and Three Conjugate Double Linkings at the Same Time. The Aliphatic Terpenes and their Derivatives. Synthesis of New αγε-Trienes. C. J. Enklaar (*Rec. trav. chim.*, 1917, **36**, 215—246. Compare A., 1909, i, 111).—In the light of the behaviour of the ozonides of ocimene and *allo*-ocimene on decomposition, the author suggests the formulæ

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$$

and $CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CHMe$, respectively, for these hydrocarbons. In support of these views, he has determined the refractometric indices of a number of unsaturated hydrocarbons, two of which are new, and compared their values with those obtained for ocimene and *allo*-ocimene.

Tiglic aldehyde, D_4^{14} 0·8723; $D_4^{9·6}$ 0·8764; n_α 1·44706, n_D 1·45117, n_β 1·46148, n_γ 1·47080 at 9·6°; $E\Sigma$ Ref., 1·17; $E\Sigma$ Disp., 45%, when mixed in anhydrous ether with allyl bromide and the mixture slowly poured on to an excess of zinc, gave *ε-methyl-$\Delta^{\alpha\epsilon}$-heptadien-δ-ol*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CHMe$, b. p. 172—173°/760 mm., $D_4^{12·2}$ 0·8766, n_α 1·46174, n_D 1·46481, n_β 1·47278, n_γ 1·47945 at 11·8°. This alcohol, when heated with potassium hydrogen sulphate (compare A., 1913, i, 243), gave a liquid which, when distilled over sodium, yielded three fractions, b. p. 78—82°/96 mm., 82—83·5°/96 mm., and 83·5—85°/96 mm. This liquid is *ε-methyl-$\Delta^{\alpha\gamma\epsilon}$-heptatriene*, the physical constants for the three fractions being: (1) $D_4^{11·2}$ 0·7891, n_α 151798, n_D 1·52595, n_β 1·54806, n_γ 1·56939 at 14·7°; (2) $D_4^{10·8}$ 0·7938, n_α 1·52475, n_D 1·53301, n 1·55618, n_γ 1·57854 at 15·3°; (3) $D_4^{11·3}$ 0·7965, n_α 1·52620,

n_D 1·53466, n_β 1·55811, n_γ 1·58114 at 15°. This hydrocarbon readily polymerises, either during distillation or in the presence of acids. Attempts at hydrogenation by means of sodium in absolute alcohol only yielded resins and a very small amount of a liquid, b. p. 133—135°. At −20° it readily absorbs two atoms of bromine, and the bromide formed slowly absorbs two more atoms of bromine. It readily absorbs oxygen and gives an *iso*nitroso-compound.

$\alpha\beta$-Methylethylacraldehyde, when treated in the same way as the tiglic aldehyde, yielded *ε-methyl-Δ^{αε}-octadien-δ-ol*,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_2Me,$$

b. p. 85·5—87°/18 mm., $D_4^{20\cdot1}$ 0·8644, n_α 1·45867, n_D 1·46177, n_β 1·46963, n_γ 1·47617 at 17·2°. This alcohol, when dehydrated with potassium hydrogen sulphate, gave *ε-methyl-Δ^{αγε}-octatriene*, obtained in three fractions, b. p. 85°/36 mm., 85—87°/36 mm., 87°/36 mm. Of these, the first and third fractions had the physical constants: (1) n_α 1·50873, n_D 1·51584, n_β 1·53568, n_γ 1·55452 at 23°; (3) n_α 1·52465, n_D 1·53349, n_β 1·55632 at 23·2°.

The specific and molecular refractions for the various lines of the principal and higher boiling-point fractions of *allo*-ocimene have been recalculated in the light of more recent work, and are tabulated. These are compared in the light of the rules of Auwers and Eisenlohr (compare A., 1911, ii, 781) against the values for certain methylbutadienes. $\Delta^{\beta\delta}$-Hexadiene, $CHMe{:}CH{\cdot}CH{:}CHMe$, b. p. 77—78°, $D_4^{12\cdot5}$ 0·7273, n_α 1·45133, n_D 1·45591, n_β 1·46800, n_γ 1·47855 at 12·5°; δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, $CMe_2{:}CH{\cdot}CH{:}CH_2$, b. p. 73·9—74·8°/750 mm., D_4^{16} 0·7229, n_α 1·44125, n_D 1·44580, n_β 1·45720, n_γ 1·46755 at 13°; isoprene, $CH_2{:}CH{\cdot}CMe{:}CH_2$, b. p. 33·8—34·3°/756 mm., D_4^{16} 0·6849, n_α 1·41818, n_D 1·42245, n_β 1·43371, n_γ 1·44367 at 13°; βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene,

$$CH_2{:}CMe{\cdot}CMe{:}CH_2,$$

D_4^{16} 0·7304, n_α 1·43486, n_D 1·43866, n_β 1·44972, n_γ 1·45832 at 13°.

These, when converted into molecular refractions and compared with the values for ocimene recalculated by using Eisenlohr's atomic constants (compare A., 1911, ii, 81), indicate that in ocimene there is a system of double linkings interrupted once in

	$E\Sigma_\alpha$.	$E\Sigma_D$.	$E\Sigma_{\beta-\alpha}$.	$E\Sigma_{\gamma-\alpha}$.
$CHMe{:}CH{\cdot}CH{:}CHMe$	1·96	2·03	52%	53%
$CMe_2{:}CH{\cdot}CH{:}CH_2$	1·36	1·44	43	49
$CH_2{:}CMe{\cdot}CH{:}CH_2$	1·14	1·20	39	45
$CH_2{:}CMe{\cdot}CMe{:}CH_2$	0·54	0·56	33	34
Ocimene	1·17	1·24	41	47

the centre by a side-chain, this being opposed to Eisenlohr's views (*loc. cit.*).

The decane which is obtained by the hydrogenation of ocimene with active nickel has b. p. 160—161°/760 mm., $D_4^{20\cdot2}$ 0·7289, n_α 1·40891, n_D 1·41103, n_β 1·41603, n_γ 1·42024 at 20·2°, these values being in agreement with those for the decane obtained from geraniol.

In a supplement to the paper, the author describes a modifica-

tion of the method of filling the tube for a lead chromate combustion for use in the analysis of volatile substances, which are difficult to burn, with which it is possible to obtain accurate results.

W. G.

The Melting Points of some Hydrocarbons, in particular of Dienes, having a System of Conjugate Double Linkings. C. J. Enklaar (*Rec. trav. chim.*, 1917, **36**, 247—249).—In an endeavour to find some relationship between the melting points of unsaturated hydrocarbons with conjugate double linkings and the corresponding saturated hydrocarbons, the author has tried to determine the melting points of nine such hydrocarbons, and finds that although these hydrocarbons, except dihydromyrcene and $\beta\zeta$-dimethyloctane, become solid and crystalline at low temperatures, they do not melt sharply, the process being spread over a rather wide range of temperature in each case. W. G.

Union of Hydrogen with Acetylenic Derivatives. Hydrogenation of Dimethyldiethylbutinenediol [$\gamma\zeta$-Dimethyl-Δ^{δ}-octinene-$\gamma\zeta$-diol]. Y. S. Zalkind and (Mlle.) V. Markarjan (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 538—550. Compare A., 1915, i, 640).—In presence of colloidal palladium, $\beta\epsilon$-dimethyl-Δ^{γ}-hexinene-$\beta\epsilon$-diol (compare A., 1914, ii, 257; 1915, ii, 435) or $\gamma\zeta$-diethyl-Δ^{δ}-octinene-$\gamma\zeta$-diol combines with two atoms of hydrogen, hydrogenation proceeding only very slowly after the formation of the ethylenic glycol. In the former case, however, the hydrogenation is quite rapid, and the velocity of the reaction is approximately proportional to the relative amount of catalyst employed. Hydrogenation of the second of the two above acetylenic glycols is much slower, and the velocity soon reaches a maximum value when the amount of catalyst is increased; thus, identical results are obtained with 0·01, 0·02, or 0·03 gram of colloidal palladium per 0·01 gram-mol. of the glycol in 30 c.c. of alcohol.

On account of these differences, the authors have now investigated the hydrogenation of $\gamma\zeta$-dimethyl-Δ^{β}-octinene-$\gamma\zeta$-diol, which occupies an intermediate position to the above two acetylenic glycols; this glycol has m. p. 54—55° (compare Dupont, A., 1914, i, 134), and not 48—49° as stated by Iocitsch (A., 1914, i, 403). Here also, in presence of colloidal palladium, two atoms of hydrogen are added, and the velocity and the manner of its variation with the quantity of palladium are intermediate to those observed in the two cases referred to above.

In ethereal solution containing platinum black, the acetylenic glycol unites with four atoms of hydrogen, and there is no break in the hydrogenation at the point corresponding with the addition of two atoms. The magnitude of k remains constant until 85—90% $2H_2$ are absorbed, and subsequently increases markedly in consequence of further hydrogenation of the saturated glycol; Dupont (*loc. cit.*), indeed, obtained $\gamma\zeta$-dimethyloctan-γ-ol in this case.

$\gamma\zeta$-Dimethyl-Δ^{δ}-octene-$\gamma\zeta$-diol, $OH\cdot CMeEt\cdot CH:CH\cdot CMeEt\cdot OH$, obtained by hydrogenation of $\gamma\zeta$-dimethyl-Δ^{δ}-octinene-$\gamma\zeta$-diol in presence of colloidal palladium, is a viscous, odourless, colourless liquid, D_4^0 0·9349, $D_4^{19\cdot6}$ 0·9216, $n_D^{19\cdot6}$ 1·45593, which does not distil unchanged, even in a vacuum. When it is acetylated, one of the hydroxyl groups is lost as water, with formation of a double linking, whilst the other undergoes normal acetylation; the *product*, $C_{12}H_{20}O_2$, b. p. 170—190°, or 100—140°/38 mm., thus represents the acetyl derivative of a diethylenic alcohol. When distilled in a vacuum, $\gamma\zeta$-dimethyl-Δ^{δ}-octene-$\gamma\zeta$-diol loses the elements of water, yielding the corresponding *oxide*, $C_{10}H_{18}O$, which was obtained pure by dehydration of the ethylene glycol with sulphuric acid, and is a mobile liquid with an odour like that of camphor, b. p. 156—158°, D_4^0 0·8592, $D_4^{13\cdot5}$ 0·8480, $n_D^{13\cdot5}$ 1·43508.

$\gamma\zeta$-Dimethyloctane-$\gamma\zeta$-diol, $OH\cdot CMeEt\cdot CH_2\cdot CH_2\cdot CMeEt\cdot OH$, obtained by hydrogenation in presence of platinum black, is a viscous, odourless, colourless liquid, D_4^0 0·9363, $D_4^{19\cdot6}$ 0·9255, $n_D^{19\cdot6}$ 1·45523. This glycol also loses the elements of water on acetylation, one hydroxyl group alone undergoing acetylation; the resulting *acetylated ethylenic alcohol*, $C_{12}H_{22}O_2$, is a liquid, b. p. 110—140°/37 mm., with a pleasant odour, and decolorises bromine and alkaline permanganate. When $\gamma\zeta$-dimethyloctane-$\gamma\zeta$-diol is distilled in a vacuum, it loses $1H_2O$, the principal product being an *unsaturated alcohol*, $C_{10}H_{20}O$, b. p. 162—165°, D_4^0 0·8364, $D_4^{13\cdot6}$ 0·8260, $n_D^{13\cdot6}$ 1·42997, which rapidly decolorises bromine water and alkaline permanganate solution; a small proportion of the γ-oxide is also formed. T. H. P.

Stability of Mercuric Lactate and its Aqueous Solutions. Preparation of Mercuric Lactate. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], **15**, 33—41).—Dry mercuric lactate may be kept for an indefinite period without undergoing decomposition, but its aqueous solution, particularly when concentrated, is less stable, the mercuric lactate changing gradually to mercurous lactate. A 0·1% solution remains almost unaltered for about three months, only 1·25% of the salt being reduced during this time, but if mercuric oxide is present, the rate of the reduction is accelerated considerably. To prepare mercuric lactate, a mixture of 100 grams of lactic acid and 400 grams of water is boiled until the residual solution weighs 320 grams (this operation decomposes any anhydride which may be present), the solution is then cooled, and 105 grams of yellow mercuric oxide are added in small quantities at a time. After one hour, the mixture is filtered, the filtrate is poured into shallow dishes, and seeded with a crystal of the salt. The crystals formed are separated, washed with small quantities of water, and dried at the ordinary temperature. Mercurous lactate may be prepared by heating 400 grams of water, 100 grams of lactic acid, and 100 grams of mercuric oxide on a water-bath for one hour, then filtering the mixture, and heating the filtrate for some hours; the mercurous lactate separates gradually as a precipitate. W. P. S.

Stereochemical Studies. II. Action of Potassium Xanthate on Salts of the Halogeno-succinic Acids. Bror Holmberg (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 8, 1—56).—Further measurements on the velocity of lactone-formation from *l*-bromosuccinic acid (compare Johansson, A., 1912, ii, 544, and Holmberg, A., 1914, i, 139) have been carried out, both with the pure potassium salt alone and in the presence of potassium nitrate. Consideration of all the results hitherto obtained shows that the velocity of lactone-formation increases only very slightly with increase in concentration of the metal ion present. There is no evidence that "cation catalysis" takes place to any considerable extent. The *l*-bromosuccinic acid used had $[\alpha]_D^{17}$ $-76·5°$.

Similar results were obtained with the potassium and strontium salts of *l*-chlorosuccinic acid; the acid had $[\alpha]_D^{16}$ $-55·7°$. The velocity of lactone-formation is much smaller than with the bromo-acid.

Pure *l*-iodosuccinic acid was prepared by the action of potassium iodide on *d*-lactonemalic acid, and had $[\alpha]_D^{15}$ $-81·3°$. For experiments on the velocity of lactone-formation, the inactive acid, prepared from *l*-bromosuccinic acid and sodium iodide in acetone solution, was used. Exact determinations could not be carried out, but the results indicated that the velocity is greater than with the bromo-acid. Retardation, however, takes place to a considerable extent, owing to the iodide formed, since the reaction

$$O'\cdot CO\cdot \overline{CH\cdot CH_2\cdot CO\cdot O} + I' = O'\cdot CO\cdot CHI\cdot CH_2\cdot CO\cdot O'.$$

is reversible.

Velocity measurements on the action of potassium xanthate on salts of bromosuccinic acid showed that xanthosuccinic acid is formed in two ways, namely: (1) By direct substitution of bromine by the xanthate residue, in accordance with the equation

$$l\text{-}CO_2M\cdot CHBr\cdot CH_2\cdot CO_2M + MS\cdot CS\cdot OEt = d\text{-}CO_2M\cdot CH(S\cdot CS\cdot OEt)\cdot CH_2\cdot CO_2M + MBr.$$

This reaction is bimolecular, and takes place slowly. (2) By addition of xanthate to the primarily formed lactonemalic acid salt, in accordance with the equations: (*a*) $l\text{-}CO_2M\cdot CHBr\cdot CH_2\cdot CO_2M \rightleftarrows d\text{-}CO_2M\cdot \overline{CH\cdot CH_2\cdot CO_2} + MBr$ (unimolecular and slow reaction),

$$(b)\ d\text{-}CO_2M\cdot \overline{CH\cdot CH_2\cdot CO_2} + MS\cdot CS\cdot OEt = l\text{-}CO_2M\cdot CH(S\cdot CS\cdot OEt)\cdot CH_2\cdot CO_2M$$

(very quick reaction). The reaction (1) is accelerated by metal ions to a much greater extent than (2*a*). The chloro- and iodo-succinic acids gave similar results, but with the former acid direct substitution played a lesser, and with the latter acid a greater, part than in the case of the bromo-acid. In the case of iodosuccinic acid, even in dilute solutions, the iodide formed during the reaction retarded the formation of xanthosuccinic acid from the lactonemalic acid, with the result that the total velocity of the

reaction between potassium xanthate and the iodosuccinates was less than when the bromosuccinates were used.

The results of the kinetic experiments necessitated a revision and extension of the author's previously published results (compare A., 1914, i, 139) on the reaction between potassium xanthate and lactonemalic acid. It is shown that the xanthate adds on to the lactonemalic acid, both in weakly acid and weakly alkaline solutions, giving a lævoxanthosuccinic acid with practically the maximum rotation. In slightly acid solution, the reaction is practically quantitative, but the yield is diminished in strongly acid solution, owing to the precipitation and decomposition of the xanthic acid; in alkaline solution, the yield is also diminished by saponification of the lactonemalic acid.

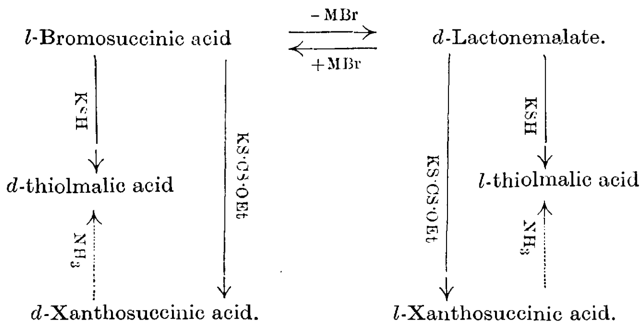
Since the addition of xanthate to the primarily formed lactonemalic acid gives *l*-xanthosuccinic acid, the formation of the *d*-acid must be ascribed to direct substitution in accordance with equation (1). It does not therefore seem any longer necessary to ascribe a special stereochemical action to "cation catalysis," all the changes which take place being explicable by the equations given above. It follows that all the factors which favour reaction (1) or retard reaction (2*a*) will make the product richer in dextro-acid or poorer in lævo-acid, and vice versa. The correctness of these conclusions is shown by reference to the author's previous paper (*loc. cit.*), and also, for example, by the following experiments, which show how necessary it is to work under well-defined conditions when investigating the Walden transformation. In a given experiment, the reaction (1) will be most in evidence at the beginning, since the concentrations of the reacting substances are then the greatest. It follows that the xanthosuccinic acid formed at the commencement of the reaction will be more strongly dextrorotatory than that formed later. This was shown to be the case when strontium *l*-bromosuccinate was used; the strontium xanthosuccinate is only sparingly soluble, and the first portions which separated out gave a dextrorotatory acid. The next fraction gave an acid which was less dextrorotatory, and the succeeding fractions gave acids which were more and more lævorotatory. Similar results were obtained with *l*-chloro- and *l*-iodo-succinic acids. Owing to the variation in the relative velocities of the reactions (1) and (2*a*) with these acids, it was found, for example, that at concentrations where the *l*-iodosuccinic acid gave *d*-xanthosuccinic acid, the *l*-bromo-acid gave a weakly, and the *l*-chloro-acid a strongly lævorotatory xantho-acid.

Temperature was found to have a very great influence on the reaction. Thus a solution which was 0·65 molar with respect to potassium *l*-bromosuccinate and potassium xanthate gave, at 0°, a xanthosuccinic acid with $[\alpha]_D$ +30·6°; at 11—12° the xantho-acid formed had $[\alpha]_D$ +8·3°, at 25° the product had $[\alpha]_D$ −13·8°, and at 40° $[\alpha]_D$ −40·1°. These big differences in the rotation of the product do not indicate that the temperature quotients of the reactions (1) and (2*a*) are very different, since calculation shows that if the velocity constant of the reaction (1) is doubled by a rise in

temperature from 15° to 25°, that of the reaction (2*a*) is thereby trebled.

Comparison of the above results with those obtained in the reaction between potassium hydrogen sulphide and potassium *l*-bromosuccinate (A., 1916, i, 307) shows that the substitution of bromine by the ·SH residue takes place quicker than the substitution by the xanthate residue. Also, since the reaction (2*a*) is the same in both cases, the total velocity of reaction should be greater with potassium hydrogen sulphide than with potassium xanthate; this was confirmed experimentally.

Since the active xanthosuccinic acids when acted on by ammonia give thiolmalic acids with the same sign of rotation, all the results hitherto obtained can be expressed by the following scheme:



Since in the decomposition by ammonia reaction does not take place at the asymmetric carbon atom, no change in configuration will take place when the xanthosuccinic acids are transformed into the thiolmalic acids. From the other reactions one can reasonably conclude that potassium bromide, hydrogen sulphide, and xanthate behave stereochemically in the same way towards lactonemalic acid, and therefore that *l*-bromosuccinic acid has the same configuration as l-mercapto- and *l*-xantho-succinic acids. It follows that *stereochemical transformation takes place in the direct substitution of bromine in bromosuccinic acid by the* ·SH *residue or the xanthate residue*, that is, in the bimolecular reaction (1). Similarly with the *l*-chloro- and *l*-iodosuccinic acids. T. S. P.

Constitution of Meconic Acid. W. Borsche (*Ber.*, 1916, **49**, 2538—2546).—Meconic acid is usually regarded as the trihydrate of a derivative of 4-pyrone, $C_7H_4O_7,3H_2O$. This being so, it should yield various derivatives of pentamethylene oxide on reduction with hydrogen in the presence of colloidal palladium (compare other 4-pyrones, A., 1915, i, 574), but instead of this it gives $\alpha\beta\gamma\epsilon$-tetrahydroxypimelic acid. It would appear, therefore, that in this case the pyrone ring is ruptured during reduction, but the nearly related, undoubted 4-pyrones, comenic acid, and pyromeconic acid, give normal pentamethylene oxide products, from which it follows

that meconic acid is most probably not a pyrone at all. It is presumed to be $\alpha\alpha\beta\epsilon\epsilon$-pentahydroxy-$\gamma$-ketopimelic acid,

$$CO_2H\cdot C(OH)_2\cdot CH(OH)\cdot CO\cdot CH_2\cdot C(OH)_2\cdot CO_2H.$$

$\alpha\beta\gamma\epsilon$-*Tetrahydroxypimelic acid* crystallises in white granules, m. p. 210—215° (decomp.), and forms a *disilver* salt. When heated with concentrated hydrochloric acid in a sealed tube at 125—145° it yields lævulic acid, which may be identified by conversion into the *phenylcarbaminohydrazone*,

$$NHPh\cdot CO\cdot NH\cdot N\colon CMe\cdot CH_2\cdot CH_2\cdot CO_2H,$$

stout, white needles, m. p. 185—186° (decomp.), by mixing the neutralised product with phenylcarbamic hydrazide hydrochloride. The dry acid also yields the *diacetate* of a *pimelodilactone*, $\begin{array}{l}CH(OAc)\cdot CH_2\cdot CH\cdot O\cdot CO\\ CO\text{——}O\text{——}CH\text{—}CH\cdot OAc\end{array}$, when heated with acetic anhydride and sulphuric acid, as prismatic tablets, m. p. 169—170°. The acid does not reduce Fehling's solution or ammoniacal silver oxide, but the mother liquor from the first reduction product contains a small amount of a powerfully reducing acid, which is probably α-hydroxy-$\gamma\delta$-diketohexoic acid, as it forms a *disemicarbazone*, $C_8H_{14}O_5N_6$, m. p. 220° (decomp.).

Comenic acid, reduced under the same conditions, yields *hexahydrocomenic acid* ($\gamma\delta$-*dihydroxypentamethylene-oxide-α-carboxylic acid*), $C_6H_{10}O_5$, which crystallises in hard needles, m. p. 172°, and forms a saturated *lactone*, $C_6H_8O_4$, b. p. 205°/18 mm., on heating.

Pyromeconic acid gives a mixture of a small amount of a tetrahydro- with much of a hexahydro-derivative. The latter may be separated in the form of its diacetate, $\beta\gamma$-*diacetoxypentamethylene-oxide*, $C_9H_{14}O_5$, a fairly mobile liquid, b. p. 138—140°/18 mm., whilst the former, β-hydroxy-γ-ketopentamethylene oxide, becomes oxidised to the diketone when its aqueous solution is heated in the air, and this may be characterised as a *di-phenylcarbaminohydrazone*, $\begin{array}{l}CH_2\cdot CH_2\cdot C\colon N\cdot NH\cdot CO\cdot NHPh\\ O\text{—}CH_2\text{—}C\colon N\cdot NH\cdot CO\cdot NHPh\end{array}$, m. p. 215—216° (decomp.).

J. C. W.

d-Mannoketoheptose, a New Sugar from the Avocado. F. B. La Forge (*J. Biol. Chem.*, 1917, **28**, 511—522).—The new sugar is obtained by aqueous extraction of the avocado pear, *Persea gratissima*. d-*Mannoketoheptose*, $C_7H_{14}O_7$, crystallises in six-sided prisms, m. p. 152°, $[\alpha]_D^{20}$ $+29\cdot17°$. It is not fermented by yeast, and does not show mutarotation. It gives a colour reaction with orcinol and hydrochloric acid like other heptoses and the pentoses. The p-*bromophenylhydrazone*, $C_{13}H_{19}O_6N_2Br$, crystallises in thin plates which are usually slightly yellow, m. p. 179°. On treatment with benzaldehyde the sugar is regenerated. The phenylosazone is identical with the osazone prepared from d-mannoaldoheptose. On reduction with sodium amalgam, d-mannoketoheptose forms d-persitol (compare Bertrand, A., 1909, i, 634) and d-β-mannoheptitol. These considerations indicate that the new sugar must be a mannoheptose, for which three structural formulæ are possible. It is possible to differentiate between them by means of the p-bromo-

phenylhydrazone derivatives. *d-α-Mannoaldoheptose-p-bromophenylhydrazone*, $C_{13}H_{19}O_6N_2Br$, has m. p. 207—208°, whilst the corresponding β-derivative is uncrystallisable. The new sugar must therefore be the *d*-mannoketoheptose represented by the configuration:

$$\begin{array}{lcccccl} & H & H & OH & OH & O & \\ OH\cdot CH_2— & C— & C— & C— & C— & C— & CH_2\cdot OH \\ & OH & OH & H & H & & \end{array}$$

Perseulose (Bertrand, A., 1908, i, 715) is shown to be *l*-galaheptose, with the structural formula:

$$\begin{array}{lcccccl} & O & H & OH & OH & H & \\ OH\cdot CH_2— & C— & C— & C— & C— & C— & CH_2\cdot OH \\ & & OH & H & H & OH & \end{array}$$

The pulp of the avocado also contains a gum which on hydrolysis yields *l*-arabinose. H. W. B.

Crystallographic and Optic Properties of Mannoketoheptose and of the Osazones of Mannoketoheptose and Mannoaldoheptose. F. E. Wright (*J. Biol. Chem.*, 1917, **28**, 523—526. Compare La Forge, preceding abstract).—For details the original paper must be consulted. The osazones of mannoketoheptose and mannoaldoheptose are identical. H. W. B.

Purification of Vegetable Fibres. G. L. Stadnikov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 301—302).—The purification of vegetable fibres (cotton, flax) to be used in the study of adsorption in general, and that of colouring matters in particular, may be effected as follows. The fibre is boiled with water, which is changed each day after boiling for eight hours, this procedure being followed until 250 c.c. of the filtered water after use leaves no residue on evaporation. The extracted fibre is left for three days covered with alcohol, which is then replaced by a fresh quantity. After another period of three days, the fibre is removed from the alcohol and washed with ether, alcohol, and water successively. The complete displacement of the alcohol by water is effected only very slowly at the ordinary temperature, since even after eight months a fresh quantity of water was found to contain alcohol after being in contact with the fibre for a few days. The process takes place far more rapidly when the fibre is boiled with successive quantities of water. T. H. P.

Synthesis of Polypeptides, in the Construction of which the Amino-acids Glycine, Alanine, Leucine, and Cystine take Part. Emil Abderhalden and Ernst Wybert (*Ber.*, 1916, **49**, 2449—2473, 2838).—The synthesis of polypeptides containing residues of the amino-acids which have striking qualitative reactions appears to be worthy of attention for at least two reasons. In the first place, a knowledge of their properties would be a valuable guide in the development of methods for the separation and isola-

tion of the polypeptides obtained by the hydrolysis of proteins, and in the second they would be useful material for studies on enzymes. A number of cystine derivatives are now described, some of them having been obtained previously by E. Fischer, and their important properties are tabulated.

For comparison with dichloroacetyl-*l*-cystine (Fischer and Suzuki, A., 1905, i, 30), the authors have made by the same process *dibromoacetyl*-l-*cystine*, $[CH_2Br \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2]_2S_2$, decomp. 160°, $[\alpha]_D^{20}$ $-107 \cdot 97°$ (alcohol), and *di-iodoacetyl*-l-*cystine*, needles, decomp. 150°, $[\alpha]_D^{20}$ $-95 \cdot 35°$. The diglycylcystine (*ibid.*) obtained from these by the action of ammonia reacts with *d*-α-bromo*iso*hexoyl chloride to form *di*-d-*α-bromo*iso*hexoyldiglycyl*-l-*cystine*, m. p. 147° (decomp.), $[\alpha]_D^{20}$ $-21 \cdot 76°$, and this yields *di*-l-*leucyldiglycyl*-l-*cystine*, when left with ammonia, as an amorphous powder, decomp. 190—213°, $[\alpha]_D^{20}$ $-72 \cdot 24°$ (in water), $-75 \cdot 45°$ (in *N*-HCl), which gives a very definite biuret reaction, and is precipitated from its aqueous solution by salt or ammonium sulphate.

Di-l-*α-bromopropionyl*-l-*cystine*, m. p. 141°, $[\alpha]_D^{20}$ $-133 \cdot 23°$, is prepared from *l*-α-bromopropionyl chloride and cystine and converted into *di*-l-*alanyl*-l-*cystine*, $1H_2O$, scales, decomp. above 205° $[\alpha]_D^{20}$ $-227 \cdot 90°$. The corresponding *di*-d-*α-bromopropionyl*-l-*cystine* crystallises in bundles of feathery needles, m. p. 142°, $[\alpha]_D^{20}$ $-96 \cdot 96°$, and the *di*-d-*alanyl*-l-*cystine* separates with $1H_2O$, $[\alpha]_D^{20}$ $-137 \cdot 40°$ (in *N*-HCl). The latter differs from the *l*-alanyl and *dl*-alanyl compounds (*ibid.*) in being almost insoluble in alcohol. It reacts with *d*-α-bromo*iso*hexoyl chloride to form *di*-d-*α-bromo*iso*hexoyldi*-d-*alanyl*-l-*cystine*, decomp. 160°, $[\alpha]_D^{20}$ $-52 \cdot 67°$, and this yields *di*-l-*leucyldi*-d-*alanyl*-l-*cystine*, decomp. 203°, $[\alpha]_D^{20}$ $-115 \cdot 29°$ (water), $-126 \cdot 77°$ (*N*-HCl), in the usual way. This pentapeptide gives a very strong biuret reaction.

Di-*l*-leucyl-*l*-cystine (Fischer and Gerngross, A., 1909, i, 367) reacts with chloro- and bromo-acetyl chlorides to form *dichloroacetyldi*-l-*leucyl*-l-*cystine*, decomp. 120°, $[\alpha]_D^{20}$ $-102 \cdot 8°$, and *dibromoacetyldi*-l-*leucyl*-l-*cystine*, decomp. 120—166°, $[\alpha]_D^{20}$ $-55 \cdot 81°$, and the latter may be converted into *diglycyldi*-l-*leucyl*-l-*cystine*, $[\alpha]_D^{20}$ $-108 \cdot 86°$ (water), $-134 \cdot 46°$ (*N*-HCl), which also gives the biuret reaction.

A further problem in connexion with the polypeptides obtained from proteins is the order in which the amino-acid residues occur. If it is possible to fix the free amino-groups by some acid residue which is not readily removed on hydrolysis, then it might be possible to say to which amino-acids in the peptide these free groups belong. Naphthalenesulphonyl residues are promising in this respect. If di-β-naphthalenesulphonyldiglycyl-*l*-cystine (Fischer and Bergell, 1902—1903) is boiled with 10% hydrochloric acid, it is hydrolysed to cystine and β-naphthalenesulphonylglycine, showing that the amino-groups of glycine are the free ones in diglycylcystine.

When the amino-acid ester mixture obtained from proteins is distilled, decomposition products containing sulphur and ammonia are formed at higher temperatures. This is largely, and perhaps exclusively, due to the cystine esters, for it is found that these

decompose in this way at above 120° in a high vacuum. *Cystine diethyl ester dihydrochloride* crystallises in bundles of silky needles.

J. C. W.

The Action of Oxalyl Chloride on some Amino-compounds. J. TH. BORNWATER (*Rec. trav. chim.*, 1917, **36**, 250—257).—A continuation of previous work (compare A., 1911, i, 617; 1916, i, 20). When ethyl sarcosinate hydrochloride is boiled in dry benzene with oxalyl chloride, *ethyl oxalyldisarcosinate*, $C_2O_2(NMe\cdot CH_2\cdot CO_2Et)_2$, m. p. 76°, is obtained. α-Bromo*iso*hexoyl chloride condenses with ethyl glycinate in dry benzene, giving *ethyl α-bromo*iso*hexoylglycinate*,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

white needles, m. p. 88°, which does not condense with oxalyl chloride in boiling benzene solution. Ethyl leucylglycinate gives, with oxalyl chloride, *ethyl oxalyldileucylglycinate*,

$$C_2O_2\left(NH<\begin{matrix}CH\cdot CH_2\cdot CHMe_2\\CO\cdot NH\cdot CH_2\cdot CO_2Et\end{matrix}\right)_2,$$

m. p. 151°.

Ethyl fumaryldiglycinate (compare Fischer and Koenigs, A., 1905, i, 31) when shaken with a 25% aqueous solution of ammonia gives *fumaryldiglycinamide*,

$$NH_2\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot CH{:}CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

thin, glistening plates, m. p. 260° (decomp.). This amide does not react with oxalyl chloride in benzene solution, probably owing to its insolubility in benzene.

Ethyl phenylalaninate hydrochloride with oxalyl chloride yields *ethyl oxalyldiphenylalaninate*, $C_2O_2[NH(CO_2Et)\cdot CH\cdot CH_2Ph]_2$, m. p. 123·5°. When ethyl phenylalaninate hydrochloride is shaken with 25% ammonium hydroxide solution it yields *phenylalaninamide*, $CH_2Ph\cdot CH(NH_2)\cdot CO\cdot NH_2$, m. p. 138—139°, which with oxalyl chloride gives 2:3:6-*triketo-5-benzylpiperazine*,

$$CH_2Ph\cdot CH<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>CO,$$

m. p. 170°.

Ethyl aspartate hydrochloride condenses with oxalyl chloride, giving *ethyl oxalyldiaspartate*,

$$C_2O_2[NH(CO_2Et)\cdot CH\cdot CH_2\cdot CO_2Et]_2,$$

white needles, m. p. 108·5°. W. G.

Preparation of Guanidine. J. SMITH SHARPE (*J. Biol. Chem.*, 1917, **28**, 399—401).—Guanidine thiocyanate is formed by heating dry ammonium thiocyanate for twenty hours at a temperature from 190° to 200°. The resulting mass is extracted with water and treated with potassium carbonate, which transforms the guanidine thiocyanate into guanidine carbonate and potassium thiocyanate. After drying, the latter substance is removed by 90% alcohol and the residual guanidine carbonate recrystallised from dilute alcohol. The yield is 15—20% of the ammonium thiocyanate employed.

H. W. B.

Lead Diethyl Compounds. SVEND MÖLLER and PAUL PFEIFFER (*Ber.*, 1916, **49**, 2441—2444).—Some of the lead diethyl compounds recently described by Grüttner and Krause (A., 1916, i, 799, 800) had also been obtained independently, by another method, by the present workers. They convert lead tetraphenyl (A., 1904, i, 544) into lead diphenyl dibromide by the action of bromine, treat this with magnesium ethyl bromide, and so obtain *lead diphenyldiethyl*, $PbEt_2Ph_2$, a colourless, highly refractive liquid, D_4^{20} 1·6435, n_D^{18} 1·5939, $n_F - n_C^{18}$ 0·02333. This yields *lead diethyl dibromide*, glistening prisms, or the dichloride, when treated with the gaseous hydracids, and these compounds, in turn, give lead dimethyldiethyl when mixed with magnesium methyl iodide solution. J. C. W.

Organo-lead Compounds. P. PFEIFFER, P. TRUSKIER, and P. DISSELKAMP (*Ber.*, 1916, **49**, 2445—2449).—Lead trialkyl haloids can be obtained by the action of the halogen hydrides on lead tetra-alkyls (compare lead triethyl chloride, A., 1904, i, 544). In this way, lead tri-*n*-propyl chloride has been prepared independently of Grüttner and Krause (A., 1916, i, 799). When this is shaken with a suspension of silver oxide in water, it gives an alkaline solution of the hydroxide, from which the *bromide*, $PbPr_3Br$, m. p. 81—82°, the snow-white *sulphate*, and the *acetate*, m. p. 116°, may be obtained. Similarly, *lead tri-n-butyl chloride*, flat needles, m. p. 109—111°, gives an alkaline hydroxide which can be used to prepare the bromide.

Polis's lead diphenyl dichloride, dibromide, and dinitrate (1887) form crystalline *additive compounds* with pyridine in the molecular proportions 1 : 4, which are similar to the tin compounds, $SnPh_2X_2,4C_5H_5N$. A *compound*, $PbPh_2Br_2,2NH_3$, also exists.
J. C. W.

New Heterocyclic Systems. III. Organo-lead Compounds. IV. Diethyl*cyclo*pentamethyleneplumbine and Products obtained by Rupturing the Ring. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1916, **49**, 2666—2675).—Through the interaction of lead diethyl dichloride and the magnesium compound of αε-dibromo- (or chloro-)pentane, the authors have isolated diethyl*cyclo*pentamethyleneplumbine, which thus places lead along with phosphorus, arsenic, antimony, and bismuth among the elements which have been introduced into ring systems during the last two years. When this compound is treated with bromine at −75°, the ring is opened and lead diethyl-ε-bromoamyl bromide,

$$C_5H_{10}Br\cdot PbEt_2Br,$$

is formed. This reacts with magnesium ethyl bromide to form lead triethyl-ε-bromoamyl, which promises to be a very interesting substance, as it contains a reactive group in one of the alkyl radicles, such organo-metallic compounds being hitherto unknown.

The magnesium compound of the αε-dihalogenopentane must be free from unchanged magnesium or dihaloid, and the lead diethyl dichloride must be pure (see A., 1916, i, 800). The authors remark that the common prejudice against alkyl chlorides in the Grignard

reaction is really unfounded, for they mostly react quite readily with magnesium that has first been etched.

*Diethyl*cyclo*pentamethyleneplumbine*, $PbEt_2:C_5H_{10}$, is a colourless, mobile oil, b. p. 111°/13·5 mm., D_4^{20} 1·6866, n_D^{20} 1·5484, $n_F - n_C$ 0·01770, with an odour reminiscent of *cyclo*hexanone. *Lead diethyl-ε-bromoamyl bromide* is a colourless, viscous oil, and *lead triethyl-ε-bromoamyl* is a colourless, mobile, stable oil, b. p. 166·8°/13 mm., D_4^{20} 1·6851, n_D^{20} 1·5374, $n_F - n_C$ 0·01663. This reacts with magnesium, and the magnesium ε-triethylplumbylamyl bromide so formed is decomposed by water with the production of *lead triethyl*-n-*amyl*, an unpleasant smelling, colourless oil, b. p. 121°/15 mm., D_4^{20} 1·4815 n_D^{20} 1·5095, $n_F - n_C$ 0·01604. The same compound can be synthesised by the action of lead triethyl bromide on magnesium *n*-amyl bromide.

If the cyclic lead compound is treated with chlorine at −75°, not only is the ring ruptured, but an ethyl radicle is also displaced, and *lead ethyl-ε-chloroamyl dichloride* is formed, in doubly-refractive lancets.

Unlike the true lead tetra-alkyls, the cyclic compound is not stable in the air, owing, no doubt, to the considerable tension in the ring. J. C. W.

The Complexity of some Organic Compounds of Mercury. EINAR BIILMANN and (MLLE.) AGNES HOFF (*Rec. trav. chim.*, 1917, **36**, 289—305).—The authors determine the degree of complexity of the organic mercury compounds by measuring the concentration of the mercury ions in a mixture of a mercury salt and the organic substance giving the organic mercury complex. This has been done in four cases, and from the results the affinities of the reactions have been calculated, using the formula

$$A = R \,.\, T \,.\, \log K.$$

The comparative results found were:

	c.	*K.*	*A.*
Allylacetic acid	$10^{9\cdot29}$	$10^{8\cdot94}$	12493
Allyl alcohol	$10^{8\cdot40}$	$10^{8\cdot10}$	11184
Crotonic acid	$10^{5\cdot01}$	$10^{4\cdot71}$	6459
Maleic acid	$10^{3\cdot79}$	$10^{3\cdot47}$	5180

c being the concentration of the mercuric ions, under the uniform conditions, *K* the equilibrium constant, *A* the affinity in gram-calories. Thus the affinity of allylacetic acid and allyl alcohol for the mercury salt is about twice as great as that of crotonic or maleic acid. W. G.

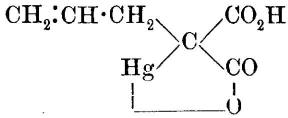
Some Complex Compounds of Platinum and Mercury. EINAR BIILMANN and (MLLE.) AGNES HOFF (*Rec. trav. chim.*, 1917, **36**, 306—312).—Potassium platinochloride reacts with unsaturated acids, in which the double linking is remote from the carboxyl group, forming complex platinum compounds. When allylacetic acid is added to an aqueous solution of potassium platinochloride a red solution is obtained which, on the addition of ammonium diamminoplatinochloride, gives a yellow, crystalline precipitate of

the *compound*, $(C_3H_5 \cdot CH_2 \cdot CO_2H,PtCl_3)_2Pt(NH_3)_4$. This compound is slowly decomposed on boiling its aqueous solution, and on the addition of potassium platinochloride gives Magnus's salt.

Allylmalonic acid under similar conditions gives a *compound*, $[C_3H_5 \cdot CH(CO_2H)_2,PtCl_3]_2,Pt(NH_3)_4$,

$PtCl_3,C_3H_5 \cdot CH(CO_2H) \cdot CO_2]Pt(NH_3)_4$,

which is also decomposed on boiling it with water.



Vinylacetic acid under similar conditions gives a yellow, crystalline precipitate, but the constitution of this has not been determined.

When allylmalonic acid (1 mol.) is added to a solution of mercuric acetate (1 mol.) in dilute acetic acid solution a white, crystalline precipitate of *hydroxymercuriallylmaleic acid anhydride* (annexed formula) is obtained. W. G.

Action of Ammonia and Calcium on Benzene. A. V. Dumanski and (Mlle.) A. V. Zvereva (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 994—996).—When dry ammonia is passed through benzene containing shavings of calcium, the following reactions take place: $Ca + 4NH_3 = Ca(NH_3)_4 = Ca(NH_2)_2 + H_2 + 2NH_3$ and $C_6H_6 + H_2 = C_6H_8$. T. H. P.

The Friedel-Crafts' Reaction. Eyvind Bœdtker and O. M. Halse (*Bull. Soc. chim.*, 1916, [iv], **19**, 444—449. Compare Radziewanowski, A., 1895, i, 129, 412).—The inverse of Friedel-Crafts' reaction, $C_6H_3R_3 + 2C_6H_6 \rightleftharpoons 3C_6H_5R$, can be brought about in the case of polyalkylated benzenes by boiling the compound with an excess of benzene and a little aluminium chloride for several hours. The only exceptions found were *m*- and *p*-xylenes, which did not give any toluene. Di- and tri-ethylbenzenes gave ethylbenzene; poly*iso*propylbenzenes gave *iso*propylbenzene; *p*-di-*tert.*-butylbenzene gave *tert.*-butylbenzene; poly-*tert.*-amylbenzenes gave *tert.*-amylbenzene, and cymene gave excellent yields of toluene and *iso*propylbenzene.

Attempts to convert dichloro- and dibromo-benzene, under the same conditions, into the monochloro- and monobromo-compounds were entirely unsuccessful, the only products being polyhalogenated benzenes. W. G.

Electrochemical Chlorination of Benzene and Toluene. Fr. Fichter and Lupu Glantzstein (*Ber.*, 1916, **49**, 2473—2487).—The chlorination of benzene and toluene at a platinum anode in concentrated hydrochloric acid has received considerable attention, but doubt has been expressed whether the products formed are due to electrochemical action or to the ordinary action of chlorine, particularly as there would seem to be no connexion between the amperage and the yield (see Cohen, Dawson, and Crosland, T., 1905, **87**, 1034; Bruner and co-workers, 1907–1909; van Name and Maryott, A., 1913, ii, 181). It is now suggested that the discordant results

are due to the lack of homogeneity in the electrolyte. Clear solutions can be obtained by adding sufficient glacial acetic acid, and experiments conducted with such electrolytes leave no room for doubt that the chlorination which takes place is really an electrochemical process. Furthermore, under these conditions, it is possible to pursue the chlorination to its utmost limits, but compounds containing oxygen are also produced.

In the case of benzene, the following products have been isolated: chlorobenzene, *p*-dichlorobenzene,*s*-tetrachlorobenzene, hexachlorobenzene, pentachlorophenol, and chloranil. Details are given of experiments on the influence of various factors on the reactions, and the isolation of the products is described. Owing to the complexity of the reactions, there is no connexion between the work done and the quantity of current or the time of the reaction. The best yield of chlorinated products is obtained with a current of 3 faradays, that is, one that provides three gram-atoms of chlorine for every gram-molecule of benzene, and comparative experiments on the influence of other factors were conducted with such a current-quantity. It is found that increasing the concentration of benzene up to the point at which an emulsion is formed (nearly 1 mol. per litre) improves the yield, but the most important factor is the current-density. Raising the amperage up to about 1 amp. per cm.^{2} increases the total yield, and also that of the more chlorinated products, and no hexachlorobenzene is formed at all if the current-density is less than 0·26 amp. per cm.^{2}. Higher temperatures are also favourable to the advanced stages of the process. The best conditions for the preparation of hexachlorobenzene are low concentration and higher amperage and temperature, and the solid separates almost completely on cooling in a very pure form. The total yield and yield of hexachlorobenzene are greater at platinum anodes than at those of graphite or magnetic oxide of iron, but at these the oxidation is much more important, about half of the product being soluble in alkali hydroxides.

In the case of toluene, the complexity of the product and the difficulty of isolating the individual compounds are hindrances to a systematic study of the reactions, but the important discovery has been made that, in the dark, at least three chlorine atoms are introduced into the nucleus before the methyl group is attacked. This is taken as very good evidence in support of Bruner's hypothesis that atomic chlorine attacks the ring and molecular chlorine the aliphatic side-chain, and the fact that the electrochemical chlorination is an almost impossible process in the aliphatic series (for example, the acetic acid used in the present mixtures is unaffected) confirms this. The compounds which have been identified, partly by isolation, partly as the products of the action of boiling water on them, are as follows: *o*- and *p*-chlorotoluene, 2:4-dichlorotoluene, 2:4:5-trichlorotoluene; pentachlorotoluene, pentachlorobenzyl chloride, and hexachlorobenzene; 2:4:5-trichlorobenzylidene dichloride (as the corresponding aldehyde) and 2:4:5-trichloro-3:6-dihydroxybenzylidene dichloride, an unstable substance. With a current of 0·005 amp. per cm.^{2}, mono- and di-

chlorotoluenes are the sole products; with 0·01 amp. per cm.^{2}, trichlorotoluene makes its appearance, but the quinol derivative, which renders the identification of the products so difficult, is not formed until the current density is at least 0·05 amp. per cm.^{2}. J. C. W.

Preparation of Nitro-compounds. A. HEINEMANN (Brit. Pat., 102216; from *J. Soc. Chem. Ind.*, 1917, **36**, 78).—Nitrosylsulphonic acid is used in place of concentrated sulphuric acid to absorb the water formed during the nitration of aromatic compounds with nitric acid. Thus *m*-dinitrobenzene (50 grams) is slowly heated with nitrosylsulphonic acid (100 grams) until dissolved; nitric acid (100 grams) is added to the solution, and the mixture is maintained at 110—120° until *s*-trinitrobenzene is formed. H. W.

The Preparation and Ionisation of the Dialkyl Hydrogen Phosphates and Benzenedisulphonic Acids. W. A. DRUSHEL and A. R. FELTY (*Amer. J. Sci.*, 1917, [iv], **43**, 57—66).—Dimethyl, diethyl, and dipropyl hydrogen phosphates were prepared by decomposing the trialkyl phosphates by the action of concentrated aqueous barium hydroxide, purifying the barium tetra-alkyl salts by crystallisation, and treating the anhydrous barium salts with the theoretical quantity of sulphuric acid. From conductivity measurements at 25° it is found that the degree of ionisation of corresponding solutions of the acid esters decreases as the weight of the alkyl group increases.

A comparison of the conductivities of the three isomeric benzenedisulphonic acids has shown that in corresponding solutions the para-acid is slightly more ionised than the meta-acid, whilst the ionisation of the ortho-acid is not nearly so great. The rates at which ethyl acetate is hydrolysed by 0·1*N*-solutions of the three acids show differences which correspond with the differences in the degree of ionisation.

The benzene-*o*- and -*p*-disulphonic acids used in these experiments were prepared from the corresponding amino-sulphonic acids by the xanthate method which has been found to give satisfactory results. H. M. D.

Polymerisation of α-Phenyl-Δ$^{\alpha\gamma}$-butadiene. S. V. LEBEDEV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 997—1008). —α-Phenyl-Δ$^{\alpha\gamma}$-butadiene polymerises into two products, one soluble, obtained on heating, and the other insoluble, obtained at the ordinary temperature in the light. The results of the author's investigations show that the dimeride of α-phenyl-Δ$^{\alpha\gamma}$-butadiene is a unicyclic hydrocarbon containing two double linkings; it combines with 2 mols. of hydrogen and with 2 mols. of ozone, and on oxidation with permanganate yields an acid, $C_{13}H_{14}O_6$, erroneously regarded by Riiber (A., 1904, i, 569) as of the formula $C_{13}H_{12}O_6$. The character of the polymerisation and the properties of the dimeride and of the polymeride indicate that, in spite of certain individual divergences, the type of the polymerisation is the same as with deriv-

atives of diphenyl with aliphatic substituents. According to the scheme previously given by Lebedev (A., 1913, i, 1285), the formation of the dimeride is expressed thus:

$$\cdot CHPh\cdot \underset{|}{C}H\cdot \underset{|}{C}H\cdot CH_2 \;.\;.\;.\;.\;.\;.\; CHPh\cdot \underset{|}{C}H\cdot \underset{|}{C}H\cdot CH_2\cdot \longrightarrow$$

$$CH{<}{\begin{matrix}CH{-\!-}CH_2\\ CHPh\cdot CH_2\end{matrix}}{>}CH\cdot CH{:}CHPh,$$

the resulting product being 2-phenyl-4-styryl*cyclo*hexene, and the acid which it gives on oxidation, α-phenylbutane-$\alpha\gamma\delta$-tricarboxylic acid.

The crude polymeride obtained by heating at 150° is a colourless, viscous liquid, and the dimeride separated by distillation in an atmosphere of hydrogen consists almost entirely of the variety with the higher boiling point. The pure dimeride has b. p. 196·5—197°/5 mm., D_4^{20} 1·0332, n_C^{20} 1·59918, n_D^{20} 1·60570, n_F^{20} 1·62346, and when hydrogenated in alcoholic solution in presence of platinum-black yields 1-*phenyl*-3-ω-*phenylethyl*cyclo*hexane*,

$$CH_2{<}{\begin{matrix}CHPh\cdot CH_2\\ CH_2{-\!-}CH_2\end{matrix}}{>}CH\cdot CH_2\cdot CH_2Ph.$$

which is a colourless, odourless liquid, b. p. 205—206°/11 mm., D_4^{20} 1·0004, n_C^{20} 1·55324, n_D^{20} 1·55787, n_F^{20} 1·56936, n_G^{20} 1·57944. In acetic acid solution complete hydrogenation takes place, the product being the *compound*, $C_{20}H_{36}$, which is a colourless, viscous liquid, b. p. 192°/8·5 mm., D_4^{20} 0·9257, n_C^{20} 1·49708, n_D^{20} 1·49963, n_F^{20} 1·50573, n_G^{20} 1·46170.

The *diozonide* of the dimeride, $C_{20}H_{20}O_6$, forms a heavy, white powder which flashes when heated. Oxidation of the dimeride with permanganate in acetone solution yields benzoic acid and α-phenylbutane-$\alpha\gamma\delta$-tricarboxylic acid (compare Thiele and Meisenheimer, A., 1899, i, 603).

The polymeride of α-phenyl-$\Delta^{\alpha\gamma}$-butadiene, $(C_{10}H_{10})_x$, is formed to the extent of 5% at 150° and forms a powdery mass coagulating at about 90°. Its behaviour towards ozone is that of polymerides of divinyl hydrocarbons, the resultant *compound*, $(C_{10}H_{10}O_4)_x$, being a white solid. The conclusion is drawn that the structure of the polymeride is represented by the scheme:

$$(\cdot CHPh\cdot CH{:}CH\cdot CH_2\cdot CHPh\cdot CH{:}CH\cdot CH_2\cdot)_x.$$

Experiment shows that compounds containing in the molecule the group CHPh:C· are able in the light to form dimerides of the *cyclo*butane type, and it is highly probable that α-phenyl-$\Delta^{\alpha\gamma}$-butadiene can yield such a dimeride under suitable conditions, these being a low temperature, diminished velocity of the divinyl type of polymerisation, and action of light. T. H. P.

Synthetic Investigations in the Indene Series. A. P. Orechov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 433—449).—This work has been already published in a slightly more condensed form (A., 1914, i, 265). T. H. P.

Preparation of Aromatic Amines and Catalysts therefor. Badische Anilin- & Soda-Fabrik (U.S. Pat., 1207802; from *J. Soc. Chem. Ind.*, 1917, **36**, 78. Compare A., 1915, i, 796).—The

hydrogen may be mixed with carbon monoxide, and a zinc compound may be used to promote the action of the copper catalyst.

H. W.

The Displacement of Sulphonic Acid Groups in Amino-sulphonic Acids by Halogen Atoms. JOHN JOSEPH SUDBOROUGH and JAMIAT VISHINDAS LAKHUMALANI (T., 1917, **111**, 41—50).—After summarising the earlier observations of the displacement of such radicles as halogen, carboxyl, acetyl, and sulphonyl by new substituents when in the 2-, 4-, or 6-position with respect to an amino- or hydroxyl group in an aromatic compound, the authors describe the results of an investigation of the action of halogens on various amino-sulphonic and amino-carboxylic acids.

It is found that with 2:6-dibromosulphanilic acid, bromine, applied as bromine water, potassium hypobromite solution, or an acidified solution of potassium bromide or bromate, effects an almost quantitative displacement of the sulphonic acid group with production of *s*-tribromoaniline and sulphuric acid in a yield exceeding 90%; a similar result is obtained with 4:6-dibromoaniline-2-sulphonic acid.

Chlorine reacts with the two isomeric dibromoanilinesulphonic acids, giving mixtures of 4-chloro-2:6-dibromo- and 2-chloro-4:6-dibromo-anilines with tribromoaniline, the formation of the latter probably being due to the displacement of an atom of bromine from one molecule of dibromo-acid and its reaction with a second molecule (compare Wegscheider, A., 1897, i, 557; Chattaway and Orton, T., 1901, **79**, 822; Orton and Reed, T., 1907, **91**, 1543).

Iodine has no action on the dibromoanilinesulphonic acids even at 100°, but a solution of iodine monochloride in acetic acid effects the displacement of the sulphonic acid group, the products being 2:6-*dibromo-4-iodoaniline* and 2:4-*dibromo-6-iodoaniline*,

$$C_6H_2Br_2I{\cdot}NH_2.$$

With the corresponding dibromoaminocarboxylic acids the carboxyl group is more difficult to displace, and whereas bromine gave good yields of *s*-tribromoaniline, chlorine and iodine monochloride effected no displacement in the case of the para- and only a very slight displacement in the case of the ortho-compound.

Comparative experiments showed that a sulphonic acid group in the ortho-position to an amino-group is more reactive than a similar group in the para-position; in the meta-position, a sulphonic acid group is quite inactive towards displacement.

For experimental details see the original paper. D. F. T.

Nitro-derivatives of Alkyltoluidines and the Relation between their Molecular Refractions and those of Similar Compounds. J. D. JANSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 564—576).—A comparison has been made of the molecular refractivities of a number of nitro-derivatives of aromatic amines, in the course of which some new compounds have been prepared.

2:3-Dinitrodimethyl-*p*-toluidine was obtained by the gradual addi-

tion of 2-nitrodimethyl-*p*-toluidine to excess of nitric acid (D 1·20) in which a little carbamide had been dissolved. After twenty-four hours water was added, and an orange-brown substance separated, which proved to be 2:3-*dinitrodimethyl*-p-*toluidine*, m. p. 87°. By oxidation with chromic acid it is converted into 2:3-dinitro methyl-*p*-toluidine. By dissolving in nitric acid and adding sodium nitrite it yields 2:3-dinitro-*p*-tolylmethylnitrosoamine, which when boiled with acetic acid gives 2:3-dinitromethyl-*p*-toluidine melting at 159°. Experiments made with ammonia, alkylamines, and aniline show that 2:3-dinitrodimethyl-*p*-toluidine does not react with these substances, and it follows that the nitro-groups are difficult to replace.

2:5-Dinitroethyl-*p*-toluidine is obtained by adding the calculated quantity of nitric acid to diethyl-*p*-toluidine dissolved in concentrated sulphuric acid and pouring into two volumes of water. It has a red colour and melts at 105°. Some 2:5-*dinitro*-p-*tolylethylnitrosoamine*, a light yellow compound melting at 84°, is formed at the same time, the two substances being separated by means of hydrochloric acid.

3:4:5-*Trinitro*-o-*tolylethylnitroamine*, m. p. 112—113°, is formed when 4-nitroethyl-*o*-toluidine is boiled for some time with nitric acid (D 1·49). It is almost colourless, and forms 3:4:5-*trinitroethyl*-o-*toluidine*, m. p. 150°, when boiled for some hours with phenol, amyl alcohol, and a little concentrated sulphuric acid.

The refractivity data show that the molecular refraction depends to a considerable extent on the position of the nitro-group with reference to that of the amino-group. If isomerides are arranged in the order of their refractivity, a series is obtained which is identical with the corresponding series for the homologues of these nitro-derivatives except in one case. The exceptional behaviour is shown by the 3:5- and 2:6-dinitro-*p*-toluidines and their dimethyl derivatives. It may be explained by anomalous dispersion, for when the absorption curves for these substances are compared it is found that the curves for the two 2:6-compounds are similar, whilst those for the two 3:5-compounds diverge greatly. H. M. D.

The Resolution of Asymmetric Quinquevalent Nitrogen Compounds. I. The Salts of *d*- and *l*-Phenylbenzylmethylallylammonium Hydroxide with *d*- and *l*-α-Bromocamphor-π-sulphonic Acid. JOSEPH REILLY (T., 1917, **111**, 20—28).—The optically active acids show greater variation with regard to the facility with which they can be employed as agents for the resolution of compounds containing asymmetric nitrogen atoms than for the resolution of similar carbon compounds. After briefly reviewing the different behaviour of the optically active acids in this respect and indicating the possible reasons why in the case of some racemic bases salt formation with certain optically active acids does not give a product capable of resolution by recrystallisation, the author describes experiments made with the phenylbenzylmethylallylammonium bromocamphorsulphonates.

Whereas *dl*-phenylbenzylmethylallylammonium iodide (Pope and

Peachey, T., 1899, **75**, 1127) is easily resolvable by conversion into the *d*- or *l*-β-camphorsulphonate, the substitution of α-bromocamphor-π-sulphonic for camphorsulphonic acid gives a much less satisfactory result. In order to ascertain whether racemisation sufficiently accounts for this difference, the author has obtained pure d-*phenylbenzylmethylallylammonium* d-*α-bromocamphor-π-sulphonate* and l-*phenylbenzylmethylallylammonium* l-*α-bromocamphor-π-sulphonate*, $[\alpha]_D$ $+81.5°$ and $-81.2°$ respectively, by the interaction of the iodide of the necessary base with the silver salt of the correct acid. In a similar manner, *d*-phenylbenzylmethylallylammonium *l*-α-bromocamphor-π-sulphonate and *l*-phenylbenzylmethylallylammonium *d*-α-bromocamphor-π-sulphonate, $[\alpha]_D$ $-20.5°$ and $+20.3°$ respectively, were prepared from the corresponding iodides and silver salts. These four salts are of the same order of stability as the corresponding β-camphorsulphonates and show very little tendency to racemise; it is therefore unlikely that racemisation is the cause of the relative difficulty of resolving *dl*-phenylbenzylmethylallylammonium iodide by means of the active α-bromocamphor-π-sulphonic acids.

For experimental details see the original paper. D. F. T.

Studies in Ring Formation. II. The Action of Aromatic Amines on Acetylacetone and Benzoylacetone. EUSTACE EBENEZER TURNER (T., 1917, **111**, 1—4. Compare A., 1915, i, 1052).—Benzoylacetone behaves similarly to acetylacetone (*loc. cit.*) towards benzidine, giving *dibenzoyl*iso*propylidenebenzidine*,

$$C_{12}H_8(N{:}CMe{\cdot}CH_2Bz)_2;$$

it also reacts with α- and β-naphthylamines, *p*-bromoaniline, and 2:6-dimethoxyaniline, forming the corresponding mono-anils, namely, *benzoylacetone-α-naphthalide*, *benzoylacetone-β-naphthalide*, $C_{10}H_7{\cdot}N{:}CMe{\cdot}CH_2Bz$, *benzoylacetone*-p-*bromoanil*,

$$C_6H_4Br{\cdot}N{:}CMe{\cdot}CH_2Bz,$$

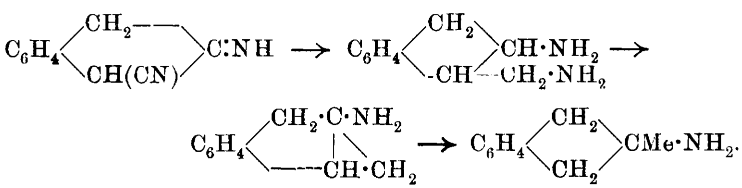
and benzoylacetone-2:6-dimethoxyanil respectively; diphenylamine is without action on benzoylacetone. The mono-anil of benzoylacetone (Beyer, A., 1887, 849) refuses to condense further with aniline, whilst the mono-anil derived from acetylacetone when heated with aniline yields no dianil, but undergoes disruption with formation of acetanilide; diacetyl*iso*propylidenebenzidine, the condensation product of acetylacetone and benzidine, also appears to be unaffected by boiling aniline.

The behaviour of β-diketones is thus seen to be very different from that of α-diketones which fairly readily yield dianils, and it also appears that the mechanism of the interaction of a β-diketone, such as benzoylacetone with the reagents mercaptan, aniline, and semicarbazide, is different in each case (see Posner, A., 1901, i, 14).

For experimental details see the original. D. F. T.

The Indene Series. III. 2-Amino-2-methylhydrindene from *o*-Xylylene Dicyanide. J. VON BRAUN, O. KRUBER, and E. DANZIGER (*Ber.*, 1916, **49**, 2642—2654).—In 1892, Zanetti obtained the expected diamine, $C_6H_4(CH_2{\cdot}CH_2{\cdot}NH_2)_2$, and another

base, $C_{10}H_{13}N$, by the reduction of *o*-xylylene dicyanide by means of sodium and alcohol. The authors anticipated that this base would contain a seven-membered ring, and be formed, therefore, by the elimination of ammonia from the diamine, as piperidine is formed from pentamethylenediamine. On investigation, however, they find that it is a primary amine, contains no ethylene linking, yields phthalic acid on oxidation, is not a tetrahydronaphthylamine. and consequently, neither of the more obvious compounds, but rather 2-amino-2-methylhydrindene. Moore and Thorpe have shown that *o*-xylylene dicyanide is readily transformed by alkalis into a cyclic iminonitrile (T., 1908, **93**, 165), and it is now found that this compound also yields the above base on reduction. It appears, therefore, that the dicyanide is either reduced directly to the diamine or first rearranged and then reduced when boiled with sodium and alcohol. Even so, the whole reduction is remarkable, and it seems to be without a parallel. The reduction of the imino-nitrile is explained by the scheme:



The two bases obtained by boiling *o*-xylylene dicyanide, in quantities as large as 100 grams at a time, with sodium and alcohol, are easily separated by distillation. *o*-Di-β-aminoethylbenzene is a colourless, almost odourless liquid, b. p. 165—170°/18 mm., which forms a *platinichloride*, a *picrate*, m. p. 219—220°, an *acetyl* compound, m. p. 190°, and a *benzoyl* derivative, m. p. 201°. It behaves in many respects more like ethylenediamine than a polymethylenediamine, giving, for example, with methyl iodide, only the *compound*, $NMe_2\cdot C_2H_4\cdot C_6H_4\cdot C_2H_4\cdot NMe_3I$, m. p. 175—185°, and not yielding a glycol on treatment with nitrous acid. It is furthermore remarkable that this glycol cannot be obtained by the other method, namely, by the reduction of the ester of the corresponding acid. *o*-Phenylenediacetic acid can be prepared readily by heating *o*-xylene dicyanide with concentrated hydrochloric acid at 110° in a sealed tube, and the *ethyl* ester, $C_6H_4(CH_2\cdot CO_2Et)_2$, has b. p. 188°/15 mm. The base is also physiologically inert, which would not be expected from its relationship to β-phenylethylamine.

2-*Amino-2-methylhydrindene* is an oil with a mild basic odour, has b. p. 118—119°/18 mm., and yields the following derivatives: *hydrochloride*, m. p. 241°, *hydrobromide*, m. p. 290—293°, *platinichloride*, decomp. 220°, *picrate*, m. p. 244°, *benzoyl* derivative, m. p. 160°, and *acetyl* compound, m. p. 127°. The *benzenesulphonyl* compound, m. p. 104°, reacts with methyl iodide in the presence of sodium ethoxide to form 2-*benzenesulphonylmethylamino-2-methylhydrindene*, m. p. 93—95°, which may be hydrolysed to 2-*methylamino-2-methylhydrindene*, b. p. 113—118°/15 mm. (*hydrochloride*,

m. p. 212°, *platinichloride*, m. p. 197°, dark yellow *picrate*, m. p. 196—198°, *benzoyl* derivative, m. p. 95—97°). This secondary base yields the *quaternary ammonium iodide*, $C_6H_4<\!\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}\!>CMe\cdot NMe_3I$, m. p. 227°, more readily than the primary amine. *2-Methyl-2-hydrindylphenylthiocarbamide*, m. p. 180°, and *di-2-methyl-2-hydrindylthiocarbamide* are readily obtained, and the base also condenses easily with aldehydes, the *salicylidene* compound having m. p. 92°.

The base is smoothly transformed into *2-chloro-2-methylhydrindene*, a faintly, pleasant smelling oil, b. p. 112—114°/15 mm., by distilling its benzoyl derivative with phosphorus pentachloride. This, or, better, the above quaternary ammonium iodide, can then be converted into *2-methylindene*, $C_6H_4<\!\begin{smallmatrix}CH_2\\CH\end{smallmatrix}\!\geqslant CMe$, which has b. p. 184—185°/741 mm., D_4^{14} 0·9897, n_D^{14} 1·57574, and forms a well-crystallised *anisylidene* compound, m. p. 120°. The production of *2-hydroxy-2-methylhydrindene* from the amine or chloro-compound is attended by difficulties which have not been overcome, but the compound can be synthesised by the action of magnesium methyl iodide on β-hydrindone. It has m. p. 52°, b. p. 132—135°/11 mm., and forms a *benzoate*, m. p. 145°.

2-Amino-2-methylhydrindene has remarkable physiological properties. It increases the blood pressure more than β-phenylethylamine, and, when injected subcutaneously, causes excitation of the motory nerve and respiratory centres in a very high degree.

J. C. W.

Isomeric Transformations in the Series of *cyclo*Hexanol and its Homologues and of *cyclo*Hexylcarbinol. N. A. Rozanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 309—321. Compare A., 1915, i, 657).—The author has investigated the action of hydriodic acid at a low temperature on *cyclo*hexanol, *cyclo*hexylcarbinol, 1-methyl-4-*cyclo*hexanol, and 1-methyl-3-*cyclo*hexanol, the action of silver nitrite on the iodides obtained, and the action of oxalic acid or acetic anhydride on the alcohols, with the object of ascertaining in which stage and under what conditions phenomena of isomerisation occur.

The action of hydriodic acid on *cyclo*hexanol yields solely *cyclo*hexyl iodide, which is converted by silver nitrite into a mixture of nitro*cyclo*hexane and 1-nitro-1-methyl*cyclo*pentane. In the action of either aqueous or anhydrous oxalic acid on *cyclo*hexanol, no isomerisation takes place, almost quantitative yields of *cyclo*hexene being obtained. *cyclo*Hexylcarbinol is convertible into the corresponding iodo-derivative, and the latter, by the action of oxygen on the magnesium compound, back again into the alcohol without isomerisation. The action of silver nitrite on this iodide, namely, ω-iodomethyl*cyclo*hexane, yields ω-nitromethyl*cyclo*hexane and 1-nitro-1-methyl*cyclo*hexane (compare Zelinski, A., 1908, i, 864).

The action of oxalic acid on *cyclo*hexylcarbinol yields methylene-

*cyclo*hexane, which undergoes further change, presumably by way of a bicyclic compound, into *cyclo*heptene:

$$CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CH_2 \longrightarrow \begin{matrix}CH_2\cdot CH_2\cdot CH\\ | \qquad\quad |\\ CH_2\cdot CH_2\cdot CH\end{matrix}{>}CH_2 \longrightarrow$$

$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ | \\ CH_2{-}CH_2{-}CH\end{matrix}{\geqslant}CH.$$

The conclusion is drawn that six-membered rings are little, if at all, more stable than those with five carbon atoms. The isomerising factors are here, also, (1) the action of halogen hydracid, but only at a high temperature, (2) nitration by means of silver nitrite, and (3) the action of oxalic acid. In the last case, this effect is exerted only at the moment of the reaction and only with primary alcohols, that is, with derivatives of carbinol. As with other rings, isomerisation of compounds with a side-chain is accompanied by enlarging of the ring, whilst that of compounds without a side-chain produces diminution of the ring.

The action of silver nitrite on 2-iodo-1-methyl*cyclo*hexane yields 1-*nitro*-1 : 2-*dimethyl*cyclo*pentane*, $CH_2{<}\begin{matrix}CH_2\cdot CMe\cdot NO_2\\ | \\ CH_2\cdot CHMe\end{matrix}$, b. p. 72—75°/45—46 mm., D_4^{20} 1·0310, n_D^{20} 1·4538; the normal product of the reaction was not obtained pure, owing to insufficiency of material. This action and that of silver nitrite on 3-iodo-1-methyl*cyclo*hexane are under investigation. T. H. P.

Nitration of *p*-Tolyl Carbonate. A. F. Holleman and (Mlle.) J. M. A. Hoeflake (*Rec. trav. chim.*, 1917, **36**, 271—280).—A quantitative study of the nitration of *p*-tolyl carbonate in sulphuric acid at 4—9°. The results show that the nitro-group enters as 96·3% in the ortho-position to the methyl group and 3·7% into the meta-position, thus indicating that the influence of the carbonate group is infinitely small in comparison with that of the methyl group. W. G.

Tetra- and Penta-methylorcinol. II. J. Herzig and F. Wenzel (*Monatsh.*, 1916, **37**, 549—565. Compare A., 1911, i, 776).—The earlier portion of the paper is devoted to a discussion of the probable structure of the bromo-derivatives $C_{11}H_{14}O_2Br_2$ and $C_{12}H_{17}O_2Br$ obtained, respectively, from tetramethyl- and pentamethyl-orcinol; the former derivative, on treatment with potassium hydroxide, yields a mixture of fumaric acid and di*iso*propyl ketone, whilst the latter gives a substance of the composition $C_{12}H_{18}O_3$ (*loc. cit.*). The chemical behaviour of this substance (see below) does not supply sufficient evidence to enable a final choice of structure, and two alternative schemes of formulation are suggested to represent the relationship with pentamethylorcinol.

[With St. Eberwein.]—Although the substance $C_{12}H_{18}O_3$ is soluble in potassium hydroxide solution without decomposition and can be recovered unchanged, prolonged treatment with boiling

potassium hydroxide solution causes the formation of two substances, one a neutral oil, $C_{11}H_{18}O$, b. p. 102—103°/15 mm., and the other a crystalline acid, $C_{11}H_{20}O_4$, m. p. 133—135° (the *methyl* ester, m. p. 38—40°, forms an *acetyl* derivative). D. F. T.

o- and *p*-**Triphenetyltelluronium Salts.** KARL LEDERER (*Ber.*, 1916, **49**, 2529—2531).—Compare other triaryltelluronium salts (A., 1916, i, 810). The new p- and o-*triphenetyltelluronium* salts are, respectively, as follows: *iodides*, rhombic needles, m. p. 208—209°, and white needles, m. p. 226—227°; *bromides*, m. p. 218° and m. p. 202—203°; *picrates*, elongated, rhombic plates, m. p. 178—179°, and cubes, m. p. 164—165°. J. C. W.

o-**Phenetyltellurium Compounds.** KARL LEDERER (*Ber.*, 1916, **49**, 2532—2538).—Di-*o*-phenetyl telluride has been obtained by the action of magnesium *o*-phenetyl bromide on tellurium dibromide (compare A., 1916, i, 208). It is not identical with the Rust-Rohrbaech product of the action of tellurium tetrachloride on phenetole (*ibid.*).

Di-o-*phenetyl telluride*, $Te(C_6H_4{\cdot}OEt)_2$, is a viscous oil, b. p. 244—244·5°/18 mm., which gives rise to the following *di*-o-*phenetyltelluronium* compounds in the usual way; *dichloride*, columns, m. p. 163—164°; *dibromide*, four-sided columns, m. p. 183—184°; *di-iodide*, deep reddish-brown needles or rhombic tablets, m. p. 214—215°; *oxide*, $TeO(C_6H_4{\cdot}OEt)_2$, short needles, m. p. 205—206°, easily oxidised by the air during its crystallisation; *methiodide*, columns, m. p. 138—140°. It also forms *additive compounds* with the mercuric haloids, as follows: *chloride*, $Te(C_6H_4{\cdot}OEt)_2,HgCl_2$, m. p. 174—175°; *bromide*, m. p. 160—161°; *iodide*, m. p. 90°. J. C. W.

α-**Naphthyltellurium Compounds.** KARL LEDERER (*Ber.*, 1916, **49**, 2663—2666).—Di-*α*-naphthyl telluride was obtained by Lyons and Bush by heating tellurium with mercury di-*α*-naphthyl (A., 1908, i, 417), but it may also be obtained by the author's general method, namely, by the action of magnesium *α*-naphthyl bromide on tellurium dibromide. It forms *additive compounds* with the mercuric haloids: *chloride*, m. p. 187—188° (decomp.); *bromide*, m. p. 178—179°; *iodide*, yellow granules, m. p. 152—153° (decomp.). *Di-α-naphthyltelluronium di-iodide* crystallises in deep red needles, m. p. 184—186°; the *oxide*, R_2TeO, is a microcrystalline powder, m. p. 224—225° (decomp.), and *di-α-naphthylmethyltelluronium iodide* has m. p. 146° (decomp.). J. C. W.

p-**Hydroxytolylsulphone.** JOSEF ZEHENTER (*Monatsh.*. 1916, **37**, 587—607. Compare A., 1912, i, 444).—When *p*-cresol is heated with fuming sulphuric acid at 170—180° for four to six hours, *p*-hydroxytolylsulphone (compare Tassinari, A., 1889, 245) is formed, together with a small quantity of di-*p*-tolyl oxide and a larger quantity of 4-cresol-2-sulphonic acid. The following derivatives of the sulphone were prepared: *sodium* derivative,

$C_{14}H_{13}O_4SNa,3\frac{1}{2}H_2O$, microscopic prisms; *potassium* derivative, not obtained crystalline; *dibenzoyl* derivative, $C_{14}H_{12}O_4SBz_2$, needles, m. p. 231—232°; *dibromo*-derivative, $C_{14}H_{12}O_4Br_2S$, colourless prisms, m. p. 185—188°; *dinitro*-derivative, $C_{14}H_{12}O_4S(NO_2)_2$, obtained by the action of diluted nitric acid (1 : 1), m. p. 222—224°; *disulphonic* acid with $6H_2O$, which could not be dehydrated further than $C_{14}H_{12}O_4S(SO_3H)_2,H_2O$, m. p. 156—158° (*potassium* salt with $4H_2O$, colourless leaflets; *sodium* salt with $5H_2O$, colourless, microscopic prisms; *barium* salt with $6H_2O$, of which only five were removable without decomposition of the salt; *lead* salt with $5H_2O$), obtained from the sulphone by the action of sulphuric acid at 100°.

When heated with sulphuric acid at 180°, the sulphone was converted into 4-cresol-2(or 6) : 3-disulphonic acid (Richter, A., 1886, 151). D. F. T.

Diaryldisulphones. O. Hinsberg (*Ber.*, 1916, **49**, 2593—2594).—Kohler and MacDonald (A., 1899, i, 904) found that the same product is obtained by treating sodium benzenesulphinate with *p*-toluenesulphonyl chloride as by the action of benzenesulphonyl chloride on sodium *p*-toluenesulphinate, and regarded this fact as evidence of the formula $R\cdot SO_2\cdot SO_2\cdot R$ for diaryldisulphones. This is supported by the preparation, in either direction, of *phenyl-β-naphthyldisulphone*, $C_{10}H_7\cdot SO_2\cdot SO_2Ph$, which crystallises in clusters of colourless needles, m. p. 166°. J. C. W.

Reaction of Ethereal Complexes of Metal Haloids with Aromatic Hydrocarbons. I. N. S. Conev (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 550—580).—The aim of the author's investigations is to procure new experimental data capable of elucidating the structure of the etherates, and the present paper contains the result of work on the etherates of stannic chloride. Emphasis is laid on the necessity of investigating the etherates in conditions which exclude the possibility of any decomposing action of atmospheric moisture. With this end in view, a special apparatus, to be described later, has been devised.

With ethyl ether, stannic chloride always forms the dietherate, $SnCl_4,2Et_2O$, m. p. 87°, no matter what the experimental conditions employed. When heated on a water-bath, the etherate decomposes into ether and stannic chloride, but at 113° its decomposition yields, in addition, ethyl chloride. Ethyl propyl ether forms only the dietherate, and the same is the case with propyl ether; the compound obtained with the latter does not give the expected results on dry distillation, and this reaction is being further investigated. *iso*Amyl ether also gives a dietherate, $SnCl_4,2(C_5H_{11})_2O$, which decomposes into its components on distillation.

Benzyl ethyl ether always yields the unstable, hygroscopic dietherate, $SnCl_4,2CH_2Ph\cdot OEt$, which can only be kept undecomposed in excess of benzyl ethyl ether. Spontaneous decomposition of this dietherate gives alcohol and a hydrocarbon, $(C_7H_6)n$, m. p.

72—75° (decomp.), which has the molecular formula $(C_7H_6)_{31}$, in freezing benzene. That this hydrocarbon is a product of the condensation of the benzyl radicle alone is shown by its formation by the action of stannic chloride on benzyl chloride (compare Zincke, A., 1871, 508, 688). It is therefore probable that benzyl chloride is an intermediate product of the decomposition of the benzyl ethyl etherate, but this could not be confirmed by direct experiment. In similar experiments with titanium chloride in place of stannic chloride, benzyl chloride was, however, isolated, and that this decomposition actually follows the above course is shown by the products it yields in presence of benzene and toluene; with the latter, the benzyl chloride formed gives the corresponding hydrocarbons. The compounds obtained in presence of benzene are: diphenylmethane, *p*- and *m*-dibenzylbenzenes, alcohol, and the compound $SnCl_4,C_6H_5Et$; that these hydrocarbons owe their formation to the intermediate formation of benzyl chloride is shown by the fact that they are obtained by the interaction of stannic chloride and benzyl chloride in benzene.

Decomposition of the benzyl ethyl etherate in toluene solution gives *p*-benzyltoluene, one or more of the isomeric dibenzyltoluenes in small proportion, and alcohol.

Benzyl methyl ether always yields the unstable dietherate, $SnCl_4,2CH_2Ph\cdot OMe$, which yields the hydrocarbon, $(C_7H_6)_n$, m. p. 73—76° (decomp.), on decomposition. When heated in benzene solution, this dietherate decomposes, giving diphenylmethane, *p*-dibenzylbenzene, and a viscid oil and an amorphous solid, which were not further investigated.

Benzyl *iso*amyl ether yields only the dietherate,

$$SnCl_4,2CH_2Ph\cdot O\cdot C_5H_{11},$$

which is stable at the ordinary temperature, but when heated undergoes decomposition in the same way as the corresponding compounds of benzyl ethyl and benzyl methyl ethers, yielding the hydrocarbon, $(C_7H_6)n$, m. p. 72—75° (decomp.). When heated in benzene solution, this etherate decomposes, yielding *iso*amyl alcohol, diphenylmethane, *p*-dibenzylbenzene, and a hydrocarbon which has a high boiling point and is similar to those obtained in other cases.

When heated in benzene solution, the etherate formed from stannic chloride and benzyl benzoate decomposes, giving diphenylmethane, *p*-dibenzylbenzene, benzoic acid, and hydrocarbons of high molecular weight. T. H. P.

Reaction of Esters with Organo-magnesium Compounds. IV. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 297—300).—The interaction of ethyl benzoate and magnesium phenyl bromide is analogous to that of methyl or benzyl benzoate (A., 1916, i, 259); if the cooling is insufficient and the whole of the ester is added at once to the organomagnesium compound, the reaction does not cease at the formation of the iodomagnesium triphenylmethoxide, but proceeds further in the direction of the formation of triphenylmethyl ethyl ether.

As would be expected from the course followed by the action of

ethyl acetate on the iodomagnesium alcoholate of benzhydrol (compare A., 1915, i, 957), the action of ethyl acetate on iodomagnesium triphenylmethoxide yields triphenylmethyl ethyl ether, but in very small yield, most of the triphenylcarbinol used being recovered unchanged; in the former reaction, both dibenzhydryl ether and benzhydryl ethyl ether are obtained, the whole of the benzhydrol reacting in these directions. This difference in behaviour in the two cases is due to the fact that the iodomagnesium alcoholate of benzhydrol is deposited as a microcrystalline powder when magnesium ethyl iodide acts on benzhydrol, and redissolves on addition of ethyl acetate (2 mols.), whereas the iodomagnesium triphenylmethoxide does not pass into solution again even when treated with a large proportion of ethyl acetate. A still lower yield of triphenylmethyl ether is obtained if the reaction is carried out in a mixture of absolute ether and benzene. T. H. P.

The Catalytic Decomposition of Benzoyl Chloride. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1916, [iv], **19**, 449—452).—When benzoyl chloride in a current of hydrogen is passed over finely divided nickel at 270—280°, there is an abundant liberation of hydrogen chloride, and the products are benzene, toluene, and diphenyl, the formation of the latter being due to the catalytic action of the nickel chloride produced. Finely divided copper under similar conditions gives benzoic anhydride, 40%, and unchanged benzoyl chloride, 60%. Barium chloride or thorium oxychloride at 420—450° give 25% of benzoic anhydride and 70% of unchanged benzoyl chloride. These two catalysts blacken, but can be regenerated by calcination. W. G.

Some Derivatives of Amino-acids. J. TH. BORNWATER (*Rec. trav. chim.*, 1917, **36**, 281—284).—*Ethyl benzoyl*-d-*aminovalerate*, $NHBz\cdot[CH_2]_4\cdot CO_2Et$, m. p. 26°, is readily obtained by passing dry hydrogen chloride into a solution of the free acid in absolute alcohol. When shaken with a 25% solution of ammonium hydroxide, it gives the corresponding *amide*, m. p. 181·5°.

Benzoyl-*d*-diaminovaleric acid gives in alcoholic solution with dry hydrogen chloride its *ethyl ester hydrochloride.*

Ethyl chloroacetylaspartate (compare Fischer and Suzuki, A., 1905, i, 121) is readily obtained by boiling chloroacetyl chloride and ethyl aspartate hydrochloride together in dry benzene solution. W. G.

Menthanecarboxylic Acids. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 862—867. Compare A., 1915, i, 420).—With the object of determining the composition of crude menthyl chloride, the author has made a preliminary examination of the menthanecarboxylic acids.

The constant menthyl chloride yields only one menthanecarboxylic acid, m. p. 65—66°, whilst crude menthyl chloride gives also a liquid acid. The action of phosphorus trichloride on the crystalline acid causes no stereoisomeric transformation, since the chloroanhydride formed may be converted again into the original acid.

Menthanecarboxylic acid, m. p. 65—66°, $[\alpha]_D$ $-54\cdot23°$ (in benzene), yields the crystalline amide, $C_{10}H_{19}\cdot CO\cdot NH_2$, m. p. 151°,

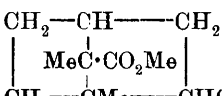
$[\alpha]_D$ $-56{\cdot}47^\circ$ (in methyl alcohol), which forms stout, prismatic crystals of the composition $(C_{11}H_{21}ON)_2,C_6H_6$; this is the only amide formed by the crystalline acid, which also gives only one anilide, $C_{17}H_{25}ON$, m. p. 152°, $[\alpha]_D$ $-70{\cdot}46^\circ$.

The liquid menthanecarboxylic acid obtained, together with the crystalline acid from crude menthyl chloride, has also been examined, but the results as yet available are insufficient to decide if the liquid acid is an individual compound or a mixture of isomerides.

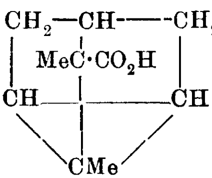
T. H. P.

An Isomeric Teresantalic Acid. H. RUPE and W. TOMI (*Ber.*, 1916, **49**, 2563—2579).—Teresantalic acid, which has been fairly completely studied by von Soden and Müller (A., 1900, i, 678), Guerbet (A., 1900, i, 242), and later by Semmler (A., 1907, i, 703, 1062; 1910, i, 573; 1911, i, 314), is of interest to the authors in connexion with work on the dependence of rotatory power on constitution. They hope to study the changes in rotation which take place as the tricyclic acid is transformed into simpler ring systems. As a preliminary, they have attempted to obtain an unsaturated acid by removing the elements of hydrogen chloride from the product of the addition of this acid to methyl teresantalate, but they have only succeeded thereby in preparing a saturated isomeride of teresantalic acid, which they designate *iso*teresantalic acid. Based on the "camphor-type" formula for teresantalic acid, the explanation offered is that the carboxyl group and the methyl group attached to the same carbon atom merely exchange positions, the former being in one case within the space bounded by the rings and outside it in the other.

Methyl teresantalate was originally obtained by the action of methyl iodide on the silver salt. Other esterification methods have now been tried in order to prepare larger quantities. For example, the *acid chloride*, b. p. 100—104°/14 mm., has been isolated by the action of thionyl chloride, but the tendency for the acid to combine with hydrogen chloride is so great that this does not give a satisfactory ester. The application of methyl sulphate, however, is quite successful. Methyl teresantalate combines with hydrogen chloride in cold alcoholic solution to form *methyl hydrochloroteresantalate* (annexed formula), which exists in two forms, α-, white leaflets, m. p. 68°, b. p. 125—127°/10 mm., and β-, which is liquid.



The corresponding *methyl hydrobromoteresantalate* is a pale yellow syrup. When these esters (better, the bromo-ester) are heated with aniline at 200—210° they yield *methyl* iso*teresantalate*, b. p. 93·5—94·5°/10 mm., from which iso*teresantalic acid* (annexed formula) is obtained by hydrolysis with alcoholic potassium hydroxide, in white crystals, m. p. 141·5°, b. p. 145—155°/12 mm. The same acid is obtained when the hydrochloroteresantalates are boiled with alco-



holic potassium hydroxide, or when the hydrobromoteresantalate is treated with zinc dust and acetic acid. The ordinary teresantalic acid, m. p. 155°, is not changed by boiling with quinoline or aniline, but the *iso*-acid loses carbon dioxide and is also partly converted into the ordinary acid. The *iso*-acid is also more soluble in water than the older acid. *Calcium*, *strontium*, and *barium* salts of each acid have been prepared.

Other experiments of a less conclusive nature are recorded. Methyl teresantalate yields a *dibromide*, without the formation of hydrogen bromide. *Teresantalanilide*, b. p. 204—205°/11 mm., is formed as a by-product in the action of aniline on methyl hydrobromoteresantalate; it changes into an *isomeride*, large, white spears, m. p. 84—86°, when boiled with alcoholic hydrochloric acid.

The chief optical constants quoted are tabulated below, choice being made of those which the authors regard as most trustworthy:

	$[\alpha]_D^{20}$.	$\lambda\alpha$.
Teresantalic acid (benzene solution)..	−76·60°	684·7 $\mu\mu$
Teresantalic acid methyl ester	−60·78	679·6
iso-Teresantalic acid (benzene)	−127·58	640·0
iso-Teresantalic acid methyl ester......	−108·75	641·0
Methyl hydrochloroteresantalate (α-form, in benzene)	−9·22	655·0

J. C. W.

The Stereochemistry of Quinquevalent Nitrogen. V. The Betaines and the Formation of Unsaturated Acids in Plants. I. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 369—390).—The unsaturated acids in plants, with the exception of certain fatty acids, are α-unsaturated compounds, and are associated with alkaloids or tertiary amines. This accords with their formation by the decomposition of betaines.

Ethyl phenyldimethylammonium acetate iodide, prepared from dimethylaniline and ethyl iodoacetate, decomposes at 103—105° and then solidifies to a mass of phenyltrimethylammonium iodide.

Benzylmethylaniline and ethyl iodoacetate yield ethyl phenylbenzylmethylammoniumacetate iodide, m. p. 115—116°. When dissolved in acetone and ethyl acetate and heated with silver *d*-camphorsulphonate on the water-bath for two hours, the *d*-camphorsulphonate of the base is obtained in white crystals of m. p. 178—179°, giving in aqueous solution $[\alpha]_D^{25}$ +13·68°. The corresponding *d*-bromide has m. p. 139—140°.

Pyridine and *l*-menthyl iodoacetate yield the *l*-iodide,

$$C_{10}H_{19}\cdot CO_2\cdot CH_2\cdot NC_5H_5I,$$

m. p. 178—179°, $[\alpha]_D^{25}$ −62·17°.

Benzylmethylaniline and *l*-menthyl iodoacetate yield phenyldibenzylmethylammonium iodide, m. p. 108·5—109°. The corresponding platinichloride has m. p. 137—138°.

The *betaine*, $\begin{array}{l}OMe\cdot C_6H_4\cdot CH_2\cdot CH-CO \\ \qquad\qquad\qquad\quad | \qquad | \\ \qquad\qquad\qquad\ NMe_3\cdot O\end{array}$ obtained by the methylation of tyrosine, forms a *picrate* melting at 171—172°. The betaine

decomposes on heating into *p*-methoxycinnamic acid and trimethylamine. The *betaine*, $\begin{array}{l}CH_2Ph\cdot CH—CO\\ \qquad\quad | \qquad |\\ \qquad\;\; NMe_3\cdot O\end{array}$, prepared by methylating phenylalanine, forms a *picrate* of m. p. 162—163° and decomposes into cinnamic acid and trimethylamine on heating.

The methylation of α-aminobutyric acid yields the *betaine*, $\begin{array}{l}CH_2Me\cdot CH—CO\\ \qquad\quad | \qquad |\\ \qquad\;\; NMe_3\cdot O\end{array}$, the *picrate* of which melts at 155—156°, whilst the betaine decomposes into α-crotonic acid and trimethylamine on heating.

Methyl iodide and potassium hydroxide convert aspartic acid into fumaric acid, trimethylamine being also formed. C. H. D.

The Border-line between Isomerism and Polymorphism. II. PAUL PFEIFFER [with J. KLINKERT and A. VON POLLITZER] (*Ber.*, 1916, **49**, 2426—2441. Compare A., 1916, i, 24).—In the earlier paper a number of nitromethoxystilbenes were described which exist in the solid state in yellow and orange forms. It now appears that two forms are only given, apparently, when the methoxyl (or a hydroxyl) group is in the para-position. As the two solids have the same melting point and give the same colour in solution, they would be regarded as dimorphic forms were it not that in many cases different additive compounds are produced by the two modifications. The most striking example of this is 2-nitro-4′-methoxystilbene-4-carboxylic acid. The yellow acid gives an orange-coloured pyridine salt, and the orange acid gives a yellow pyridine salt, the acids being recoverable by means of hydrochloric acid. In fact, it is possible to pass through a cycle of changes, thus: the yellow acid forms an orange salt which changes into the yellow salt on treatment with an excess of pyridine (owing to partial solution taking place), and this yellow salt yields the orange acid, which changes into the yellow acid on heating. The kind of isomerism here exhibited cannot be explained by the prevailing theories, and is termed "cryptoisomerism."

2-*Nitro*-2′-*methoxystilbene*-4-*carboxylic acid*,

$$OMe\cdot C_6H_4\cdot CH\colon CH\cdot C_6H_3(NO_2)\cdot CO_2H,$$

from the corresponding nitrile (*ibid.*, p. 26) is a greenish-yellow powder, m. p. 230°, which forms a pale yellow *potassium* salt, $1H_2O$, a *pyridine* salt, flat, transparent, yellow needles, and *additive compounds* with acetic acid, golden-yellow needles, and dichloroacetic acid, golden-yellow leaflets. 4-*Nitro*-2-*cyano*-2′-*methoxystilbene*, from *p*-nitro-*o*-toluonitrile and *o*-methoxybenzaldehyde, crystallises in golden needles, m. p. 146—148°. 2-*Nitro*-4-*cyano*-3′-*methoxystilbene*, from *o*-nitro-*p*-toluonitrile and *m*-methoxybenzaldehyde, forms greenish-yellow, glistening needles, m. p. 163—164°, and may be hydrolysed to 2-*nitro*-3′-*methoxystilbene*-4-*carboxylic acid*, yellow needles, m. p. 240°, which gives an orange-yellow *potassium* salt, $0{\cdot}5H_2O$, and a golden-yellow *sodium* salt, $2H_2O$.

The yellow and red *pyridine* salts of 2-nitro-4′-methoxystilbene-4-carboxylic acid (*ibid.*) are described above. The acid also forms yellow *aniline*, *quinoline*, and *diethylamine* salts, which give the

orange-coloured forms of the acid on treatment with hydrochloric acid.

4-Nitro-4'-methoxystilbene-2-carboxylic acid, from the nitrile (*ibid.*), crystallises in golden-yellow, glistening needles, m. p. 215°, combines with $1H_2O$, forms a *barium* salt, golden needles, a *potassium* salt, yellow leaflets, and gives two *pyridine* salts, a yellow variety (acid to base = 1 : 1) crystallising from cold solutions in the base, and an orange variety (2 : 3) from warm solutions. Both salts yield the yellow acid on acidifying. The corresponding *amide*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_3(NO_2){\cdot}CO{\cdot}NH_2$, obtained by condensing *p*-nitro-*o*-toluamide with anisaldehyde, has m. p. 255°.

2-Nitro-4-cyano-4'-acetoxystilbene, from *o*-nitro-*p*-toluonitrile and *p*-hydroxybenzaldehyde followed by acetylation of the resinous product, has m. p. 186°. *4-Nitro-2-cyano-4'-hydroxystilbene* forms golden-yellow needles, m. p. 226°, and yields an *acetate*, m. p. 176°. *2-Nitro-4'-dimethylaminostilbene-4-carboxylic acid*, from the nitrile (*ibid.*), crystallises in almost black, broad, flat needles, m. p. 263°, which yield a yellow *hydrochloride* and a dark red potassium salt.

J. C. W.

β-Camphorylidenepropionic Acid (Methylenecamphoracetic Acid). H. Rupe and E. Burckhardt (*Ber.*, 1916, **49**, 2547—2563).—It was recently shown that chloromethylenecamphor is a reactive substance capable of giving rise to many camphor derivatives, and several alkyl and alkylidene compounds were then described (A., 1916, i, 409). An attempt has now been made to condense the substance with ethyl sodioacetoacetate in order to obtain ultimately a diketone, thus:

$$C_8H_{14}<\begin{matrix}C{:}CHCl\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}CH{\cdot}CH(COMe){\cdot}CO_2Et\\ |\\ CO\end{matrix} \longrightarrow$$

$$C_8H_{14}<\begin{matrix}C{:}CH{\cdot}CH_2{\cdot}COMe\\ |\\ CO\end{matrix}$$

The product obtained, however, is ethyl β-camphorylidenepropionate, which suggests that the intermediate acetoacetate is so unstable that alcoholysis takes place, and the acetyl group is eliminated as ethyl acetate. The properties and reactions of the new ester and the corresponding acid form the subject of the present paper.

A solution of sodium ethoxide is gradually added to a well-stirred mixture of chloromethylenecamphor and ethyl acetoacetate at 60°, and then, after heating for a further hour or two and removing the alcohol, the residue is just acidified and extracted with ether. On distillation (12 mm.), ethyl acetate, ethyl acetoacetate, chloromethylenecamphor, and ethoxymethylenecamphor are collected in small quantities in the order named, and then the main fraction, *ethyl β-camphorylidenepropionate*,

$$C_8H_{14}<\begin{matrix}C{:}CH{\cdot}CH_2{\cdot}CO_2Et\\ |\\ CO\end{matrix},$$

is obtained as a fairly viscous, highly refractive oil, b. p.

173—174°/12 mm., or 291°/737 mm. (slight decomposition), D_4^{20} 1·0417, the yield being about 70%. The residue crystallises in slender, yellow needles, m. p. 265—267°, and is apparently *αγ-dicamphorylidenepropane*, $CH_2(CH{:}C_{10}H_{14}O)_2$.

β-Camphorylidenepropionic acid is obtained after hydrolysing the ester with cold, concentrated hydrochloric acid, in well-developed, rhombic crystals ($a:b:c=0·6414:1:1·2472$), m. p. 106°. It absorbs bromine, is oxidised by ozone to camphorquinone, and is reduced by sodium amalgam to a borneol *derivative*,

$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot CH_2\cdot CO_2H\\ |\\ CH\cdot OH\end{array},$$

white leaflets, m. p. 51—52°, b. p. 196—198°/13 mm., which will be investigated more fully. The failure to saturate the ethylene linking in the βγ-position is, of course, quite normal, but an attempt was made to saturate the chain by first displacing this linking into the αβ-position. When, however, for this purpose, the acid (or ester) is boiled or shaken with concentrated potassium hydroxide, the elements of water are first attached, and the product is the *lactone* of the *β-hydroxycamphorylpropionic acid* so formed, thus:

$$C_8H_{14}<\begin{array}{l}C(OH)\cdot CH_2\cdot CH_2\cdot CO_2H\\ |\\ CO\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C\cdot CH_2\cdot CH_2\\ |\quad\diagdown\quad\;\; |\\ CO\;\; O-CO\end{array}$$

The lactone has m. p. 207° (decomp.), and is oxidised by ozone to a substance, m. p. 210—211°, soluble in sodium carbonate, but not to camphorquinone. The *silver* and *barium* salts of the hydroxy-acid are described.

If the ester or acid is dissolved in concentrated sulphuric acid, it is supposed that the elements of water are again attached, that a δ-lactone is produced with the camphor residue in the enolic form, and more water eliminated, thus:

$$C_8H_{14}<\begin{array}{l}C\cdot CH(OH)\cdot CH_2\cdot CO_2H\\ \|\\ C\cdot OH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C\cdot CH{:}CH\\ \|\qquad\quad |\\ C-\!\!-O\cdot CO\end{array}.$$

The *lactone* which results crystallises in long, silky needles, m. p. 66°, b. p. 162—163°/10 mm., has a penetrating odour, absorbs bromine, forming a *compound*, $C_{13}H_{15}O_2Br$ (scales, m. p. 104—105°), and does not yield camphorquinone on treatment with ozone.

The acid readily loses carbon dioxide on heating at 160°, yielding ethylidenecamphor, b. p. 101—102°/10 mm., m. p. 20—22°, $[\alpha]_D$ +203·4° (*ibid.*).

The acid also reacts with diazonium salts in alkaline solutions, being in this respect also analogous to β-benzylidenepropionic acid, but the products have much greater tinctorial properties. Benzenediazonium chloride yields "*formazyl methylenecamphor*,"

$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot C\cdot N{:}NPh\\ |\qquad\quad\;\; \|\\ CO\qquad N\cdot NHPh\end{array},$$

as a red powder, m. p. 152—154°, and diazobenzenesulphonic acid gives a dye which colours silk pale wine-red and wool "tango" shades. J. C. W.

Lichen Products. II. Synthesis of Rhizonic Acid. ADOLF SONN (*Ber.*, 1916, **49**, 2589—2593).—2:6-Dinitro-*p*-xylene (A., 1916, i, 391) is converted into 2-nitro-*p*-xylen-6-ol (Kostanecki, 1886), and this is methylated by means of methyl sulphate. The 2-*nitro*-6-*methoxy*-p-*xylene*, very long, stout needles, m. p. 62—62·5°, is then reduced to the *hydrochloride* of the base, $C_9H_{13}ON,HCl,H_2O$, long, silky needles, m. p. 250—251° (decomp.), and this is converted into the monomethyl ether of β-orcinol. This is transformed into 1-*hydroxy*-6-*methoxy*-5-*aldehydo*-p-*xylene* by means of anhydrous hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride (glistening, thin prisms, m. p. 136°), and when this aldehyde is acetylated, oxidised, and hydrolysed again, the corresponding acid is obtained,

$$OH\cdot C_6HMe_2(OMe)\cdot CO_2H,$$

which proves to be identical with naturally occurring rhizonic acid. J. C. W.

Crystallographical and Optical Observations on some Organic Compounds. G. AMINOFF (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 4, 1—15).—Details are given in connexion with the crystallographical and optical constants of the following compounds: acetophenone, chloroacetophenone, bromoacetophenone, benzoylacetiminoethyl ether [$COPh\cdot CH_2\cdot C(:NH)\cdot OEt$], and cyanoacetophenone. The morphological relation between the first four substances is shown by their axial ratios ($a:b:c$), which are respectively: 1·0428 : 1 : ?, β = 111°10′, 0·9957 : 1 : 0·4270, 0·9713 : 1 : 0·4348, and 1·2962 : 1 : 0·5962. Acetophenone is monoclinic, whereas the other three substances belong to the rhombic system. Cyanoacetophenone is probably monoclinic, but well-developed crystals could not be obtained. T. S. P.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. IV. Action of Alcoholic Potassium Hydroxide Solution on Halogeno-aminobenzophenones. P. J. MONTAGNE (*Rec. trav. chim.*, 1917, **36**, 258—270. Compare A., 1908, i, 988; 1913, i, 55; this vol., i, 35).—A continuation of the study of the influence of substituents on the reduction of benzophenone to benzhydrols by alcoholic potassium hydroxide. A single amino-group in the meta-position hinders, although to a less extent than two amino-groups in the meta-positions, the reducing action of alcoholic potassium hydroxide. The introduction of one or more halogen atoms in the para-position is sufficient to neutralise this influence. A number of such halogenated compounds, namely, 4-chloro-, 4-bromo-, 4′-chloro-, 4′-bromo-, 4 : 4′-dichloro-, and 4 : 4′-dibromo-3-aminobenzophenones, have been prepared and studied. In the case of the 4-chloro- and 4 : 4′-dichloro-3-aminobenzophenones, there was only slight replacement of the halogen during the reaction, but with

the others the replacement was more marked. Except in the case of 4-chloro-3-aminobenzhydrol, alcoholic potassium hydroxide causes a more or less marked displacement of the halogen in the halogenated -3-aminobenzhydrols.

The following new compounds are described: 4-*chloro-3-aminobenzhydrol*, needles, m. p. 74·75° (corr.); 4-*bromo-3-aminobenzophenone*, from the corresponding nitro-compound, crystallises in monoclinic prisms [F. M. JAEGER, $a:b:c=1\cdot9883:1:1\cdot1745$; $\beta=86°58'$], b. p. 254·5°/17 mm., m. p. 85° (corr.), and yields 4-*bromo-3-aminobenzhydrol*, needles, m. p. 78·5° (corr.); 4'-*bromo-3-aminobenzophenone*, m. p. 135° (corr), b. p. 250°/11 mm., yields 4'-*bromo-3-aminobenzhydrol*, m. p. 87·25° (corr.); 4:4'-*dibromo-3-aminobenzophenone* has m. p. 149·75° (corr.), and gives 4:4'-*dibromo-3-aminobenzhydrol*, m. p. 116·75° (corr.).

4'-*Chloro-3-aminobenzophenone*, b. p. 235—237°/10 mm., m. p. 116·5° (corr.), gives 4'-*chloro-3-aminobenzhydrol*, m. p. 92° (corr.); 4:4'-dichloro-3-aminobenzophenone (compare Montagne, A., 1902, i, 472) yields 4:4'-*dichloro-3-aminobenzhydrol*, m. p. 94° (corr.).

W. G.

Condensation of Acetone with Imines. CHARLES MAYER (*Bull. Soc. chim.*, 1916, [iv], **19**, 452—456. Compare A., 1905, i, 214, 357, 429).—The three benzylidenetoluidines do not behave like benzylideneaniline when mixed in cold alcoholic solution with acetone. Benzylidene-*o*-toluidine does not react. Benzylidene-*m*-toluidine gives a *compound*, $C_{24}H_{23}ON$, white crystals, m. p. 181°, which, from the fact that it does not reduce a cold acetone solution of potassium permanganate, does not condense with phenylcarbimide and is not decomposed by piperidine, the author considers to be 2:6-*diphenyl*-1-m-*tolylpiperid-4-one*. Benzylidene-*p*-toluidine under the above conditions, gives, with acetone, β-p-*toluidino*-β-*phenylethyl styryl ketone*,

$$C_7H_7\cdot NH\cdot CHPh\cdot CH_2\cdot CO\cdot CH{:}CHPh,$$

pale yellow crystals, m. p. 138°, which readily reduces potassium permanganate, gives *phenyl*-p-*tolylcarbamide*, prismatic needles, m. p. 226°, with phenylcarbimide, and is decomposed in boiling alcoholic solution by a few drops of piperidine, giving distyryl ketone and *p*-toluidine. Piperonylideneaniline at the end of several months gives, with acetone in alcoholic solution, a *compound*, felted, yellow needles, m. p. 188°, which dissolves in sulphuric acid to a magenta solution, the colour disappearing on addition of water, and is not decomposed in boiling alcoholic solution by piperidine. Piperonylideneaniline gives with styryl methyl ketone in alcoholic solution a *compound*, m. p. 170°, dissolving in sulphuric acid to a reddish-yellow solution, the colour disappearing on the addition of water.

W. G.

The Friedel-Crafts' Reaction. I. Phthalyl Chloride and the Mechanism of its Reaction with Benzene. MAURICE COPISAROW (T., 1917, **111**, 10—20).—It is already known that the condensation of phthalyl chloride with benzene in the presence of

aluminium chloride gives rise to diphenylphthalide as main product, with some anthraquinone, *o*-benzoylbenzoic acid, and diphenylanthrone, and that at low temperatures *o*-benzoylbenzoic acid becomes the chief product (Scheiber, A., 1913, i, 976). The author has now discovered the formation also of phenyloxanthranol, and *tetraphenylmethane-o-carboxylic acid*, both of which are also obtainable by the interaction of diphenylphthalide with benzene. These results, together with the work of Ott (A., 1912, i, 828), Scheiber (A., 1913, i, 976), Meyer (A., 1904, i, 747), and Copisarow and Weizmann (A., 1915, i, 687), indicate the condensation to be of complex character due to the tendency of the phthalyl chloride and of its condensation products to assume cyclic structure and to the capacity of the cyclic compounds to undergo further condensation with benzene.

Haller and Guyot (A., 1899, i, 221) attributed the formation of diphenylanthrone to the presence of phthalylene chloride in the phthalyl chloride, but evidence is now adduced to show that all the above-mentioned compounds are produced in the condensation of phthalyl chloride and benzene. The mechanism of the formation of each of the compounds is considered, and equations are given representing the probable reactions in each case with indications of the most favourable conditions.

For experimental details see the original paper. D. F. T.

3 : 4-Benzofluorenone. PAUL PFEIFFER (*Ber.*, 1916, **49**, 2425).—The author obtained a ketone (A., 1907, i, 931) from a polymeride of ethyl phenylpropiolate which he suggested might be *allo*chrysoketone (3:4-benzofluorenone). Comparing it with the account of this substance recently given by Schaarschmidt (A., 1916, i, 731), the assumption is found to have been correct. J. C. W.

The Relationships of the Polymeric Ketens to *cyclo*-Butane-1 : 3-dione and its Derivatives. G. SCHROETER [with H. KESSELER, O. LIESCHE, and R. F. MÜLLER (*Ber.*, 1916, **49**, 2697—2745).—Various dimeric ketens have been formulated as derivatives of *cyclo*butane-1:3-dione, and dimeric keten itself is usually regarded as this parent diketone (compare Staudinger, and Chick and Wilsmore, T., 1910, **97**, 1978—2000). True derivatives of the *cyclo*diketone have now been prepared, in addition to dimethyl*cyclo*butane-2:4-dione (A., 1907, i, 533), by synthesis from dialkylacetonedicarboxylates, and they are found to differ in important respects from the dimeric ketens. Genuine *cyclo*butane-1:3-dione has not yet been prepared in this way, but the author prophesies that it will prove to be different from dimeric keten. Indeed, Chick and Wilsmore themselves expressed some doubt as to the cyclic nature of this substance (*loc. cit.*, p. 1982). The main differences between dimeric keten and dialkyl*cyclo*butane-2:4-diones are as follows: (i) dimeric keten is a liquid with an unbearable odour; dialkyl*cyclo*butanediones are odourless solids; (ii) dimeric keten gives no simple ketone derivatives; dialkyl*cyclo*butanediones give monophenylhydrazones and dioximes; (iii) dimeric keten forms ethyl acetoacetate when treated with alcohol containing a trace of

sodium ethoxide; the diketones form normal salts in aqueous or alcoholic solutions when treated with metallic oxides or carbonates.

The last-named reaction of a keten offers another explanation of the conversion of ethyl acetate into ethyl acetoacetate, involving the transformation of the ester into a keten form, thus:

$$CH_3\cdot CO_2Et \xrightarrow{Na} CH_2{:}C{<}^{ONa}_{OEt} \xrightarrow{MeCO_2Et}$$

$$CH_3\cdot C\begin{cases}ONa\\OEt\\CH_2\cdot CO_2Et\end{cases} \xrightarrow{EtOH} CH_3\cdot C\begin{cases}ONa\\CH\cdot CO_2Et\end{cases}$$

Dimeric ketens can, however, change into true *cyclo*butanediones (see Staudinger, A., 1911, i, 306, etc.), and therefore the chemistry of these substances is complicated by the possibility of depolymerisation, and of internal rearrangement into unimolecular compounds which may be identical with or similar to the genuine *cyclo*butanediones or the products left on the rupture of their rings.

I. *Syntheses of Dialkylacetonedicarboxylates.*—Useful directions for the preparation of methyl and ethyl acetonedicarboxylates and of the free acid from citric acid are given.

The following dialkyl derivatives were obtained from these esters by the action of the alkyl haloids in the presence of sodium methoxide solution: *methyl dimethylacetonedicarboxylate*,

$$CO(CHMe\cdot CO_2Me)_2,$$

b. p. 125°/9 mm., and the corresponding *ethyl* ester, b. p. 128°/12 mm.; *ethyl diethylacetonedicarboxylate*, b. p. 150°/12 mm.; *ethyl di*iso*propylacetonedicarboxylate*, b. p. 162°/16 mm.; and *ethyl diallylacetonedicarboxylate*, b. p. 150°/15 mm. A diphenylacetonedicarboxylate could not be obtained in this way, and therefore an attempt was made to synthesise one by the action of methyl carbonate on dibenzyl ketone in the presence of sodium suspended in ether. In this reaction, however, the synthesis stops at the first phase, the product being *methyl αγ-diphenylacetoacetate*,

$$CH_2Ph\cdot CO\cdot CHPh\cdot CO_2Me,$$

which crystallises in long needles, m. p. 59—60°. This may also be prepared by the action of sodium methoxide on methyl phenylacetate, and it yields 1 : 3-dihydroxy-2-phenylnaphthalene when dissolved in concentrated sulphuric acid (compare Volhard, A., 1897, i, 423).

II. *Condensation of the Dialkylacetonedicarboxylates to Dialkyl*cyclo*butanedionecarboxylates and Dialkyloxydialkylpyrones.*—When the above esters are carefully stirred into cold sulphuric acid monohydrate they yield the acidic diketones and feebly basic pyrones as by-products. The latter are produced by the elimination of water from ketenoid forms of the esters, thus:

$$CO{<}^{CR{:}C(OEt)\cdot OH}_{CR{:}C(OEt)\cdot OH} \longrightarrow CO{<}^{CR{:}C(OEt)}_{CR{:}C(OEt)}{>}O.$$

Methyl dimethylacetonedicarboxylate yields *methyl* 1 : 3-*dimethyl*cyclo*butane*-2 : 4-*dione*-1-*carboxylate*, $CHMe{<}^{CO}_{CO}{>}CMe\cdot CO_2Me$, m. p. 156—157°, and 2 : 6-*dimethoxy*-3 : 5-*dimethyl*-1 : 4-*pyrone*, in

bundles of large prisms, m. p. 165°. If fuming sulphuric acid is used (13% SO_3) an unstable *compound*, $CO_2Me\cdot CHMe\cdot C\begin{matrix}\diagup O\cdot SO_2\cdot O \\ \diagdown CMe-CO\end{matrix}$, m. p. 67—68°, is formed as well.

Diethyl dimethylacetonedicarboxylate gives *ethyl* 1 : 3-*dimethyl*-cyclo*butane*-2 : 4-*dione*-1-*carboxylate*, m. p. 133—135° (compare A., 1907, i, 533), and 2 : 6-*diethoxy*-3 : 5-*dimethyl*-1 : 4-*pyrone*, m. p. 87—88°. *Ethyl* 1 : 3-*diethyl*cyclo*butane*-2 : 4-*dionecarboxylate* forms long needles, m. p. 101·5—102·5°, and the *methyl* ester has m. p. 113·5—116°. The latter was prepared from a crude methyl diethylacetonedicarboxylate, b. p. 140—144°/12 mm., obtained by oxidising methyl β-hydroxy-αα′-diethylglutarate, b. p. 143°/16 mm., with chromic acid, this ester being produced by the interaction of zinc, methyl α-bromobutyrate, and methyl formate.

Ethyl diallylacetonedicarboxylate yields *ethyl* 1 : 3-*diallyl*cyclo*butane*-2 : 4-*dione*-1-*carboxylate*, m. p. 105—107·5°.

III. *Transformations and Rupture of the Ring in the Series of Dialkyl*cyclo*butanedionecarboxylates*.—When boiled with water, methyl dimethyl*cyclo*butanedionecarboxylate loses carbon dioxide and changes into *methyl β-keto-α-methylvalerate*, b. p. 80°/12 mm., which condenses with phenylhydrazine to form 1-*phenyl*-4-*methyl*-3-*ethylpyrazole*-5-*one*, $CO\begin{matrix}\diagup NPh-N \\ \diagdown CHMe\cdot CEt\end{matrix}$, m. p. 111·5°.

Trialkylacetonedicarboxylates are formed when the alkyl haloids are boiled with alcoholic solutions of the sodium salts of the dialkyl*cyclo*butanedionecarboxylates, thus:

$$CMe\begin{matrix}\diagup CO-\!\!-\!\!- \\ \diagdown C(ONa)\end{matrix}\!\!>\!CMe\cdot CO_2Et + EtI + EtOH =$$
$$CO_2Et\cdot CMeEt\cdot CO\cdot CHMe\cdot CO_2Et + NaI.$$

Ethyl δ-methylhexan-γ-one-βδ-dicarboxylate has b. p. 150°/15 mm.; *ethyl δ-benzylpentan-γ-one-βδ-dicarboxylate* has b. p. 195—196°/14 mm.; *ethyl ε-ethylheptan-δ-one-γε-dicarboxylate* has b. p. 163°/13 mm.; *ethyl ε-methylheptan-δ-one-γε-dicarboxylate* has b. p. 152°/15 mm.; and *ethyl ε-benzylheptan-δ-one-γε-dicarboxylate* has b. p. 206—207°/15 mm.

Ethyl dimethyl*cyclo*butanedionecarboxylate reacts with pure hydrazine hydrate to form 4-*methylpyrazole*-5-*one*-3-α-*propionhydrazide*, $CO\begin{matrix}\diagup NH-N \\ \diagdown CHMe\cdot C\cdot CHMe\cdot CO\cdot NH\cdot NH_2\end{matrix}$, m. p. 212—213°, but with dilute methyl-alcoholic hydrazine hydrate to form the *azine*, $\left(\begin{matrix}CO_2Et-\!\!-\!\!-CHMe \\ NH_2\cdot NH\cdot CO\cdot CHMe\end{matrix}\!>\!C\right)_2N_2$, in long needles, m. p. 134°.

Methyl dimethyl*cyclo*butanedionecarboxylate reacts with aqueous hydroxylamine to form 4-*methyl*isoo*xazole*-5-*one*-3-α-*propionhydroxamic acid*, $CO\begin{matrix}\diagup O-\!\!-\!\!-N \\ \diagdown CHMe\cdot C\cdot CHMe\cdot CO\cdot NH\cdot OH\end{matrix}$, in rosettes of prisms, with $1H_2O$, m. p. 152—153° (decomp.).

Ethyl diethyl*cyclo*butanedionecarboxylate is converted by warming with aniline into *ethyl heptan-δ-one-γε-dicarboxanilate*, $CO_2Et\cdot CHEt\cdot CO\cdot CHEt\cdot CO\cdot NHPh$, needles, m. p. 83°.

Ethyl diethyl*cyclo*butanedionecarboxylate decomposes on distillation in a high vacuum, into ethyl diethylacetonedicarboxylate and an equal weight of a non-volatile resin.

When *p*-nitrobenzenediazonium acetate solution is added to a cold alkaline solution of ethyl dimethyl*cyclo*butanedionecarboxylate the p-*nitrobenzeneazo*-compound is precipitated, m. p. 152—153·5°; this dissolves in sodium hydroxide with a deep red colour, but *ethyl hydrogen* p-*nitrobenzeneazodimethylacetonedicarboxylate*, m. p. 195·5—196°, is obtained on acidifying the solution, thus:

$$CO_2Et\cdot CMe{<}{\substack{CO\\CO}}{>}CMe\cdot N{:}N\cdot C_6H_4\cdot NO_2 \longrightarrow$$
$$CO_2Et\cdot CHMe\cdot CO\cdot CMe(CO_2H)\cdot N{:}N\cdot C_6H_4\cdot NO_2.$$

Further experiments had for their object the introduction of a second carboxyl group into the *cyclo*butanediones. This is achieved by the action of ethyl chloroformate on the sodium salts, suspended in toluene and just sufficient alcohol, or on the esters dissolved in pyridine. It is found that the esters do not react with sodium in benzene or toluene solutions, which suggests that in the free state they are true diketones, and not keto-enols, as used to be supposed. The *sodium* salt of ethyl dimethyl*cyclo*butanedionecarboxylate is a white powder. *Ethyl diethyl*cyclo*butanedionedicarboxylate* has b. p. 162—163°/1 mm., and yields ethyl diethyl*cyclo*butanedionecarboxylate when left with sodium ethoxide solution. *Methyl dimethyl*cyclo*butanedionedicarboxylate* crystallises in felted needles or stout prisms, m. p. 52—53°, b. p. 130°/0·2 mm. This solid ester, and to a lesser extent the oily ethyl ester, are remarkably stable towards water, for scission of the ring only takes place slowly even on heating. Some doubt might exist as to whether these esters conform to formula (I) or (II):

$$CO_2R\cdot CR{<}{\substack{CO\\CO}}{>}CR\cdot CO_2R \qquad\qquad CO_2R\cdot CR{<}{\substack{C\cdot O\cdot CO_2R\\CO}}{>}CR$$

(I.) (II.)

To decide this question, the esters were treated with bromine in the expectation that absorption would take place or not, as the case might be. The reaction is very complex, however, for an atom of bromine is found to enter the molecule and alkyl to be eliminated from a carboxyl group as alkyl bromide. The products lose carbon dioxide and hydrogen bromide on heating, and the whole process is explained on the assumption that formula I is correct, thus:

$$CO_2R\cdot CR{<}{\substack{CO\\CO}}{>}CR\cdot CO_2R \xrightarrow{+Br_2} CO_2R\cdot CR{<}{\substack{COBr\\CO\cdot CRBr\cdot CO_2R}} \xrightarrow{-RBr}$$
$$CO_2R\cdot CR{<}{\substack{CO\text{———}O\\CO\cdot CRBr\cdot CO}} \xrightarrow{heat}$$
(III.)
$$CO_2R\cdot CR{<}{\substack{CO\\CO}}{>}C{:}CH_2 \text{ (or } C_2H_4) + HBr + CO_2.$$

The methyl *compound* conforming to III has m. p. 158—160°, the ethyl *compound*, m. p. 41·5—42·5°.

IV. *Degradation of the Dialkyl*cyclo*butanedionecarboxylates to Dialkyl*cyclo*butanediones.* When methyl dimethyl*cyclo*butanedionecarboxylate is heated with milk of baryta, some diethyl ketone passes away in the steam, and the barium salt of dimethyl*cyclo*butane-1:3-dione remains in the solution, both "ketone" and "acid" hydrolysis taking place, thus:

$$CO_2Me\cdot CMe{<}{}^{CO}_{CO}{>}CHMe \rightarrow CHMe{<}{}^{CO}_{CO}{>}CHMe \text{ and } COEt_2.$$

The diketone has been briefly described already (A., 1907, i, 533). It decomposes silver carbonate, but when the silver salt is treated with hydrogen sulphide in ethereal suspension, no desmotropic form of the diketone is produced. The enolic form seems to be incapable of separate existence. Dimethyl*cyclo*butane-1:3-dione also forms a *phenylhydrazone*, $C_6H_8O{:}N\cdot NHPh$, yellow needles, m. p. 160°, and a *dioxime*, m. p. 196—198° (decomp.), and it may be produced, although not readily, by Staudinger's method from α-bromopropionyl bromide through methylketen. *Diethyl*cyclo*butane-1:3-dione*, prepared in the same way from ethyl diethyl*cyclo*butanedionecarboxylate, has m. p. 76—78°, forms a *silver* salt, $C_8H_{11}O_2Ag$, white leaflets, and a *phenylhydrazone*, m. p. 132·5—133·5°.

V. *Comparison of Dimeric Ketens with the Synthetic* cyclo*Butanedione Derivatives.*—The main purpose of this section of the paper is to show that dimeric ketencarboxylic esters are depolymerised and then combine with the elements of alcohol when a small shaving of sodium is added to the alcoholic solutions. The dimeric ketens are mostly obtained by heating aliphatic diazo-compounds in xylene or amyl ether (compare Staudinger, A., 1916, i, 847—856). For example, *dimeric methyl methylketencarboxylate*,

$$(CO_2Me\cdot CMe{:}CO)_2,$$

m. p. 94—96°, from methyl diazoacetoacetate, yields methyl methylmalonate. It also combines with aniline, forming a *compound*, m. p. 83—85°, probably of the formula

$$CO_2Me\cdot CHMe\cdot CO\cdot CMe(CO_2Me)\cdot CO\cdot NHPh,$$

and not identical with *methyl methylmalonanilate*,

$$CO_2Me\cdot CHMe\cdot CO\cdot NHPh,$$

m. p. 83—86°, for a mixture of these has m. p. 65—75°. Similarly, the brown oil left after heating ethyl diazobenzoylacetate with xylene can be converted into ethyl phenylmalonate, and dimeric keten itself into methyl or ethyl acetoacetate according to the alcohol chosen.

The decomposition of diazodiacetylmethane, diazobenzoylacetylmethane, diazoacetone, and diazoacetophenone was also studied, but no indications of the presence of mono- or di-meric ketens or *cyclo*butanedione derivatives in the products could be obtained.

J. C. W.

Synthesis of Hydroxyquercetin. MAXIMILIAN NIERENSTEIN (T., 1917, **111**, 4—10).—A description of the synthesis of hydroxyquercetin (Nierenstein and Wheldale, A., 1912, i, 42) on the lines

of that of quercetin (Kostanecki, Lampe, and Tambor, A., 1904, i, 517).

1 : 2 : 3 : 5-Tetrahydroxybenzene (phentetrol), prepared by a convenient modification of Oettinger's method (A., 1895, i, 457), was converted into 2 : 3 : 4 : 6-*tetrahydroxyacetophenone*,

$$C_6H(OH)_4\cdot COMe,$$

by heating with acetic acid in the presence of zinc chloride; this product, by treatment with methyl sulphate, gave, successively, 2 : 6-*dihydroxy*-3 : 4-*dimethoxyacetophenone*,

$$C_6H(OMe)_2(OH)_2\cdot COMe,$$

and 2-*hydroxy*-3 : 4 : 6-*trimethoxyacetophenone*,

$$OH\cdot C_6H(OMe)_3\cdot COMe,$$

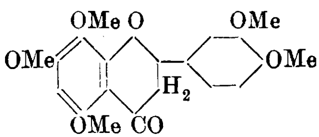
together with smaller quantities of *tetramethoxyacetophenone*, $C_6H(OMe)_4\cdot COMe$, and 6-*hydroxy*-2 : 3 : 4-*trimethoxyacetophenone*. 2-Hydroxy-3 : 4 : 6-trimethoxyacetophenone, of which the constitution was confirmed by oxidation to 3 : 4 : 6-*trimethoxy*-2 : 5-*quinoacetophenone*, $OMe\cdot C{<}{}^{C(OMe)\cdot CO}_{CO\cdot C(OMe)}{>}C\cdot COMe$, and conversion of this into 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxyacetophenone*,

$$C_6(OMe)_3(OH)_2\cdot COMe,$$

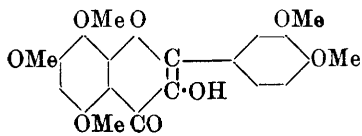
by heating with zinc dust and acetic anhydride, followed by hydrolysis, was made to undergo condensation with veratraldehyde in the presence of alkali, with formation of 2-*hydroxy*-3 : 4 : 6-*trimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone*,

$$OH\cdot C_6H(OMe)_3\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2;$$

this substance, when heated with hydrochloric acid, underwent intramolecular condensation to 5 : 7 : 8 : 3′ : 4′-*pentamethoxyflavanone* (I), which was then successively converted into 3-*oximino*-5 : 7 : 8 : 3′ : 4′-*pentamethoxyflavanone*, $C_{20}H_{21}O_8N$, and



(I.)



(II.)

5 : 7 : 8 : 3′ : 4′-*pentamethoxyflavonol* (II). Demethylation of the last substance by heating with hydriodic acid yielded a product identical with the hydroxyquercetin already described (*loc. cit.*), the formula for hydroxyquercetin being thus shown to be that given in formula II with hydroxyl substituted throughout for methoxyl.

1 : 2 : 3 : 5-Tetrahydroxybenzene was also submitted to the action of potassium hydrogen carbonate in an atmosphere of carbon dioxide (compare Clibbens and Nierenstein, A., 1915, i, 1062), with formation of 2 : 3 : 4 : 6-tetrahydroxybenzoic acid; the *tetra-acetyl-*, *tetrabenzoyl-*, and *tetramethoxy*-derivatives of this acid were prepared, as also were the *methyl* ester and acid *chloride* of the tetramethoxy-acid.

For details the original paper should be consulted. D. F. T.

Oxidation of Camphenilone. S. S. NAMETKIN, (MLLE.) E. A GREKOVA, and (MLLE.) A. M. CHUCHRIKOVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 453—455).—Camphenilone exhibits marked stability towards oxidising agents, the only definite oxidation product yet obtained being oxalic acid. When heated with dilute nitric acid in a sealed tube, fenchone is converted into secondary and tertiary nitro-derivatives (compare Konovalov, A., 1904, i, 257). The authors find that, when camphenilone is heated with nitric acid (D 1·1) in a sealed tube at 140—145°, the products consist of: (1) crystals, m. p. 90—92°, (2) an oil, and (3) *iso*-camphoronic acid. Compounds (1) and (2) are formed in very small proportions, and are probably tertiary nitroketones, two isomerides being possible in this case. The formation of *iso*-camphoronic acid is in complete accord with the accepted formula for camphenilone, and it is probable that the first phase of the oxidation yields α-nitroketone, which then undergoes hydrolysis, and subsequently further oxidation. T. H. P.

Composition of Crude Menthyl Chloride. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 867—879).—By the action of phosphorus pentachloride on menthol, Berkenheim (A., 1892, 866) prepared an optically inactive menthyl chloride which, when heated with potassium acetate and acetic acid, is partly converted into menthene and partly remains unchanged; the unchanged portion being lævorotatory, the other portion must be dextrorotatory. The various samples of menthyl chloride obtained by the author with the help of phosphorus pentachloride or by heating menthol with hydrochloric acid are lævorotatory in all cases, the magnitude of the rotation varying within wide limits, but being always less than that of the constant menthyl chloride; besides the latter, these samples may contain, therefore, either an inactive chloride or one with a low lævorotation.

In order to throw light on the composition of crude menthyl chloride, the author has investigated two different preparations, both obtained by the action of phosphorus pentachloride on menthol in light petroleum and having (1) b. p. 90—95°/16 mm., $\alpha_D = -10·68°$ in a 20 cm. tube, and (2) b. p. 91—96°/16 mm., $\alpha_D = -14·50°$ in a 20 cm. tube. Each of these samples was repeatedly heated with alcoholic potassium hydroxide, the volatile products being removed after each treatment and the undecomposed menthyl chloride again heated with the alcoholic alkali. The rotations of the different fractions of the crude menthyl chloride decomposed in this way are calculated on the supposition that the rotation of a mixture of menthyl chlorides is an additive magnitude; the accuracy of this supposition is shown by actual experiment. The rotation for the successive fractions at first increases and then diminishes, and in the second case actually changes its sign from positive to negative.

Since it is found that the constant menthyl chloride, even when mixed with those obtained by the combination of menthene with

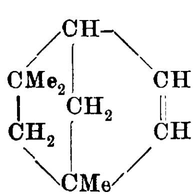
hydrogen chloride, is not decomposed on heating with alcoholic potassium hydroxide, the results of the experiments on fractional hydrolysis of the crude menthyl chloride are explainable on the assumption that the latter contains the constant menthyl chloride, two unstable, secondary, stereoisomeric chlorides with rotations of opposite sign, and an optically inactive tertiary chloride. The view expressed by various authors (compare Kursanov, A., 1915, i, 420) that crude menthyl chloride consists of a mixture of one tertiary and only two secondary chlorides must, therefore, be regarded as erroneous. From the numerical results of the experiments on fractional hydrolysis, the proportions of constant menthyl chloride in the two samples examined are calculated to be 47·31% and 44·44% respectively.

The stereoisomeric relations of these compounds are discussed, and it is shown that the supposition that, in the process of isomerisation of menthol on its conversion into chloride, a part is played by Δ^3-menthene, explains the occurrence of all the spacial and structural isomerides proved or assumed to be present in crude menthyl chloride; this explanation is therefore regarded as probable.

T. H. P.

Fenchylene, a New Synthetic Terpene. S. S. NAMETKIN and (MLLE.) A. K. RUSHENCEVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 450—452).—None of the unsaturated hydrocarbons (fenchenes) yet obtained from the near derivatives of fenchane contain the unaltered bicyclic system of fenchane. If Semmler's configuration for fenchane is accepted, it is clear that such hydrocarbons cannot theoretically be derived from fenchyl alcohol. From *iso*fenchyl alcohol, such compounds are, however, derivable, and for the terpenes which retain the original fenchane ring-system and thus differ from the fenchenes, the name "fenchylenes" is suggested. The action of zinc chloride on *iso*fenchyl alcohol (compare Bertram and Helle, A., 1900, i, 398) yields *Dd*-fenchene (compare Wallach, A., 1908, i, 809), the dehydration being accompanied by profound isomerisation. In order to avoid such isomeric change, the authors have effected the removal of the elements of water from *iso*fenchyl alcohol by Tschugaev's xanthate method (A., 1904, i, 327).

Methyl iso*fenchylxanthate* was obtained as a viscous, yellow oil. About one-third of this ester withstands a temperature of 230°, but the remainder decomposes readily at 170—180°, yielding the *fenchylene* (annexed formula), which is a volatile liquid with a faint but characteristic odour recalling that of fenchene, b. p. 139—140°/760 mm., D_4^{20} 0·8381, n_D^{20} 1·4494, $[\alpha]_D$ −68·76° (in alcohol). With bromine the hydrocarbon unites energetically, and it yields a crystalline *nitroso-chloride*, $C_{10}H_6$·NOCl, m. p. 131°. Oxidation of fenchylene by means of alkaline permanganate gives *cis*-fenchocamphoric acid (compare A., 1916, i, 269) in 77% yield.



T. H. P.

Adsorption of Alkannin in Different Solvents. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 716—718).—A solution of alkannin (anchusic acid) in light petroleum is completely decolorised by animal charcoal, the adsorption being irreversible; similar results are obtained with solutions of the ammonium and sodium salts. In aniline solution, either cold or hot, alkannin is not adsorbed, even by animal charcoal, and when the specific gravity and viscosity of the liquid are lowered by addition of ether, decolorisation is incomplete, only that part of the alkannin dissolved in the ether being adsorbed.

T. H. P.

The Pigments of Molasses and De-saccharification Residues. II. H. STOLZENBERG (*Ber.*, 1916, **49**, 2675—2677. Compare A., 1916, i, 829).—The residue left after separating the pigment contains a considerable quantity of an *acid*, $C_{34}H_{40}O_{15}N_2$, which is a very bitter, hard, black wax, to which the adhesive properties of molasses are largely due. This may be isolated after removing substances which can be benzoylated, as, for example, the remainder of the pigment. J. C. W.

The Chemical Constituents of Bituminous Tar Oils Rich in Sulphur (Ichthyol Oils). II. HELMUTH SCHEIBLER (*Ber.*, 1916, **49**, 2595—2600. Compare A., 1916, i, 65).—The author comments on the interesting connexion between his conclusions that the ichthyol oils contain thiophen derivatives and Friedmann's recent discoveries that such compounds can be obtained by the action of sulphur on straight-chain hydrocarbons (A., 1916, i, 735). The association of free sulphur and hydrogen sulphide with asphalt and ichthyol–shale deposits is quite common.

It is suggested that the constitution of thiophens may be elucidated by taking advantage of the fact that potassium attacks them on heating, forming potassium sulphide and an organo-potassium compound which may be converted into an unsaturated acid.

J. C. W.

Sulphides with Four-membered Rings. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880—901).—The action of sodium sulphide on $\alpha\gamma$-dibromopropane, $\alpha\gamma$-dibromobutane, and $\beta\delta$-dibromopentane gives rise to the formation of cyclic sulphides with four-membered rings, but the yields of these compounds are very small. In their chemical characters, such sulphides resemble those of the aliphatic series.

Trimethylene sulphide, $CH_2{<}{\overset{CH_2}{\underset{CH_2}{}}}{>}S$, obtained from $\alpha\gamma$-dibromopropane and sodium sulphide, is a colourless, highly mobile liquid with an unpleasant, penetrating odour, b. p. 93·8—94·2°/752 mm., D_4^{23} 1·0284, n_D^{23} 1·5059. It is accompanied by the polymeride, m. p. about 85°, obtained by Mansfeld (A., 1886, 525; 1887, 122) and by Autenrieth and Wolff (A., 1899, i, 579). With mercuric chloride it forms a white, microcrystalline *compound*, $C_3H_6S,HgCl_2$, which begins to contract at about 93—95° and then decomposes without melting. It yields a *methiodide*, $C_3H_6S,2MeI$, which forms colour-

less needles, m. p. 98·5—99°, and probably has the structure $C_3H_6:SMe_2I_2$, the two atoms of iodine being precipitable by means of silver nitrate. When oxidised by permanganate, trimethylene sulphide yields *trimethylenesulphone*, $CH_2<\substack{CH_2\\CH_2}>SO_2$, which crystallises in needles, m. p. 75·5—76°. The action of alcoholic ammonia on trimethylene sulphide in a sealed tube at 200° gives *γ-aminopropyl mercaptan*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot SH$, which yields a *platinichloride*, $(C_3H_9NS)_2,H_2PtCl_6$, the latter forming a pale orange powder decomposing without melting at 155—160°. Attempts to convert trimethylene sulphide into (1) the alcoholic mercaptan, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot SH$, by the action of water, and (2) trimethylene oxide by the action of silver oxide, were unsuccessful.

For the preparation of allylcarbinol, conditions have been found which give yields almost double those obtained by Pariselle (A., 1909, i, 282; 1910, i, 353); the product obtained by the author has b. p. 112·5—113·5° (corr.)/755 mm., $D_4^{17.5}$ 0·8379, $n_D^{17.5}$ 1·4146. The *phenylurethane*, $C_{11}H_{13}O_2N$, forms colourless needles, m. p. 23·5—24·5°.

2-*Methyltrimethylene sulphide*, $CH_2<\substack{CHMe\\CH_2}>S$, obtained from αγ-dibromobutane, is a colourless, highly mobile liquid with an unpleasant odour, b. p. 105·5—107·5° (corr.)/747 mm., D_4^{20} 0·9571, n_D^{20} 1·4831; it is accompanied by the polymeric sulphide, which is a yellow, amorphous powder, and by the halogenated thio-ether (?). It forms a *methiodide*, $C_4H_8S,2MeI$, which crystallises in colourless needles, m. p. 123—124°, and an additive *mercuric chloride* compound, $C_4H_8S,HgCl_2$, which begins to contract at 103—104° and at a higher temperature decomposes without melting. When oxidised with permanganate, it gives 2-methyltrimethylenesulphone, $CH_2<\substack{CHMe\\CH_2}>SO_2$, which is a colourless, viscous, almost odourless liquid with a bitter taste, b. p. 251·5—253·5° (corr.), $D_4^{16.5}$ 1·2174, $n_D^{16.5}$ 1·4700.

2:4-*Dimethyltrimethylene sulphide*, $CH_2<\substack{CHMe\\CHMe}>S$, obtained from βδ-dibromopentane, is a colourless, highly mobile liquid with a faintly terpenic odour, b. p. 112·5—113·5° (corr.)/757 mm., D_4^{18} 0·8710, n_D^{18} 1·4502. With mercuric chloride it forms a *compound*, $C_5H_{10}S,HgCl_2$, m. p. 90—91°, and oxidation with permanganate converts it into 2:4-*dimethyltrimethylenesulphone*, $C_5H_{10}:SO_2$, which is a colourless, viscous liquid, b. p. 255—255·5° (corr.)/758 mm., $D_4^{17.5}$ 1·1589, $n_4^{17.5}$ 1·4653. T. H. P.

Sulphides with Five-membered Rings. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901—928).—Tetrahydrothiophen (compare von Braun and Trümpler, A., 1910, i, 274), prepared by the action of sodium sulphide on αδ-dibromobutane or αδ-di-iodobutane (compare Hamonet, A., 1901, i, 247), is a colourless, mobile liquid with an intense odour, b. p. 118—119°, D_4^{18} 0·9607, n_D^{18} 1·4871. With mercuric chloride it forms the *com-*

pound, $C_4H_8S,HgCl_2$, which crystallises in long, slender needles, m. p. 124·5—125·5°, and, when oxidised with permanganate, it yields the corresponding *sulphone*, $\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}\!\!>SO_2$, which forms an almost odourless, viscous, bitter liquid, b. p. 285—288° (corr.)/743 mm., 153—154° (corr.)/18 mm., $D_4^{18\cdot2}$ 1·2723, $n_D^{18\cdot2}$ 1·4833, or long needles, m. p. 8—10°, and exhibits normal cryoscopic behaviour in water. When distilled through a glass tube at a dull red heat, tetrahydrothiophen undergoes partial conversion into thiophen.

[With L. NEKRITSCH.]—2-Methyltetrahydrothiophen (compare von Braun, A., 1911, i, 75), obtained by the action of sodium sulphide on $\alpha\delta$-dibromopentane in aqueous alcoholic solution, is a colourless, mobile liquid with a disagreeable odour, b. p. 132·5—132·6° (corr.)/750 mm., D_4^{18} 0·9564, n_D^{15} 1·4886. With mercuric chloride it forms a *compound* which decomposes, without melting, at about 150°. Its *methiodide*, $C_4H_7Me⁚SMeI$, forms long, slender, colourless needles, and, in the open, volatilises without melting at 151—152°, but in a sealed capillary has m. p. 155° (decomp.). When oxidised with dilute nitric acid, 2-methyltetrahydrothiophen yields the *sulphoxide*, $C_4H_7Me⁚S⁚O$, which is a viscous, slightly coloured liquid with an unpleasant odour and an intensely bitter taste. Permanganate, however, converts 2-methyltetrahydrothiophen into the *sulphone*, $C_4H_7Me⁚SO_2$, which is a colourless, viscous liquid, b. p. 279—280° (corr.)/758 mm., D_4^{14} 1·2070, n_D^{14} 1·4801, and has the normal molecular weight in freezing water.

3-*Methyltetrahydrothiophen*, $\begin{matrix}CHMe\cdot CH_2\\ | \\ CH_2\text{—}CH_2\end{matrix}\!\!>S$, obtained by the action of sodium sulphide on $\alpha\delta$-dibromo-β-methylbutane in alcoholic solution, is a colourless, mobile liquid resembling analogous sulphides in taste and odour, b. p. 137·5—138·5° (corr.)/740 mm., $D_4^{18\cdot5}$ 0·9596, $n_D^{18\cdot5}$ 1·4886. With mercuric chloride it forms a *compound*, $C_5H_{10}S,HgCl_2$, m. p. 82—83°.

meso-2 : 5-*Dimethyltetrahydrothiophen*, $\begin{matrix}CH_2\cdot CHMe\\ | \\ CH_2\cdot CHMe\end{matrix}\!\!>S$, obtained by the action of sodium sulphide on the *meso*-form of $\beta\epsilon$-dibromohexane (compare Wislicenus, A., 1901, i, 664), forms a colourless, mobile liquid of disagreeable odour, b. p. 142—142·2° (corr.)/756 mm., D_4^{0} 0·9391, $D_4^{21\cdot5}$ 0·9175, D_4^{100} 0·8415, $n_D^{21\cdot5}$ 1·4752. Its *methiodide*, $C_4H_6Me_2⁚SMeI$, forms slender needles, volatilising without melting at 156—158°. On oxidation it gives (1) with dilute nitric acid, the *sulphoxide*, $C_4H_6Me_2⁚SO$, which is a viscous, pale yellow liquid with a disagreeable odour, or (2) with permanganate, the *sulphone*, $C_4H_6Me_2⁚SO_2$, which is a colourless, almost odourless, viscous liquid, b. p. 277·5—278° (corr.)/749 mm., D_4^{18} 1·1532, n_D^{18} 1·4772, and exhibits normal cryoscopic behaviour in water. The *compound* with mercuric chloride melts at 109—110° to a turbid liquid and decomposes on further heating.

[With S. GALPERIN.]—2-*Iodo*-3 : 5-*dimethylthiophen*, $\begin{matrix}CH⁚CMe\\ | \\ CMe{=}CI\end{matrix}\!\!>S$,

prepared by the action of iodine on 3:5-dimethylthiophen in benzene solution containing mercuric oxide, forms a pale yellow liquid, b. p. 119—120·5°/20 mm., D_4^{22} 1·7474, n_D^{22} 1·6058. From this compound, by way of the organo-magnesium derivative, 3:5-dimethylthiophen-2-carboxylic acid (compare Zelinski, A., 1887, 921; 1888, 939) was prepared. Reduction of the latter by means of sodium amalgam yields 3:5-*dimethyltetrahydrothiophen-2-carboxylic acid*, $\begin{matrix} CH_2 & \text{——} & CHMe \\ | & & \\ CHMe\cdot CH(CO_2H) & & \end{matrix}\!\!>\!S$, which forms colourless needles, m. p. 98·5—99·5°; its *silver* salt was analysed. T. H. P

Sulphides with Six-membered Rings. E. Grischkevitsch-Trochimovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 928—943).—[With O. Cykina.]—Pentamethylene sulphide (compare von Braun and Trümpler, A., 1910, i, 274), obtained in good yield by the action of sodium sulphide on $\alpha\epsilon$-dibromopentane, forms a colourless, mobile liquid, resembling other cyclic sulphides in odour, b. p. 141·5—142° (corr.)/747 mm., D_4^{18} 0·9943, n_D^{18} 1·5046; its structure is confirmed by its non-identity with 2:4-dimethyltrimethylene sulphide or with 2- or 3-methyltetrahydrothiophen (see preceding abstracts). It does not undergo isomeric change when heated in a sealed tube at 200°. Its *methiodide*, $C_5H_{10}S,MeI$, forms thin, colourless needles volatilising, without melting, at 162°, and its *compound* with mercuric chloride, $C_5H_{10}S,HgCl_2$, shining, silvery plates, m. p. 137·5°, resembling boric acid crystals. In solution in carbon tetrachloride it combines with bromine, giving the highly unstable *dibromide*, $C_5H_{10}{:}SBr_2$. Dilute nitric acid converts it into the *sulphoxide*, $C_5H_{10}{:}SO$, which is obtained as a transparent, vitreous, hygroscopic mass. Oxidation with 4% permanganate solution transforms it into the *sulphone*, $C_5H_{10}{:}SO_2$, which forms shining, prismatic crystals, m. p. 98·5—99°, belonging to the monoclinic system, and has the normal molecular weight in freezing water.

2-*Methylpentamethylene sulphide*, $CH_2\!<\!\begin{matrix} CH_2\cdot CHMe \\ CH_2\text{——}CH_2 \end{matrix}\!>\!S$, prepared by the action of sodium sulphide on $\alpha\epsilon$-dibromohexane in alcoholic solution, forms a colourless liquid, b. p. 151·4—151·6° (corr.)/750 mm., D_4^0 0·9616, $D_4^{18\cdot5}$ 0·9449, $n_D^{18\cdot5}$ 1·4884, and has the normal vapour density. In chloroform solution it combines readily with bromine (2 atoms), but the product is extremely unstable. Its *methiodide*, $C_6H_{12}S,MeI$, forms thin, white needles and sublimes without melting at 158—159°; the sulphide combines also with ethyl iodide, but the reaction is very slow and the product highly hygroscopic. The *compound* with mercuric chloride, $C_6H_{12}S,HgCl_2$, forms slender needles, m. p. 97—98°. The corresponding *sulphoxide*, $C_6H_{12}S{:}O$, is a pale yellow, viscous liquid, which decomposes on distillation. The *methyl hydroxide* derivative, $C_6H_{12}SMe\cdot OH$, obtained by the action of silver oxide on the methiodide in aqueous solution, is a colourless, viscous liquid; it colours litmus and rapidly absorbs carbon dioxide from the air with formation of a crystalline carbonate. The *sulphone*, $C_6H_{12}SO_2$, forms long needles or transparent prisms, m. p. 68—68·5°, b. p. 295—296·5° (corr.)/749 mm.,

and has the normal molecular weight in boiling ether. No isomeric change occurs when the sulphide is heated in a sealed tube at 225°.

The action of hydrogen bromide on diallyl yields the crystalline *meso*-$\beta\epsilon$-dibromohexane, m. p. 38—39°, and also a liquid dibromohexane, b. p. 108—116°/15 mm. Treatment of the latter with sodium sulphide yields a sulphide, $C_6H_{12}S$, and investigation of this and of the corresponding methiodide, mercuric chloride compound, and sulphone indicates that the liquid dibromo-derivative is a mixture composed principally of $\alpha\epsilon$-dibromohexane. In the formation of this compound from diallyl, the additions of the two mols. of hydrogen bromide take place in different ways:

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + 2HBr = CHMeBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br.$$

T. H. P.

Hexamethylene Sulphide. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 944—950).—$\alpha\zeta$-Dibromohexane, $C_6H_{12}Br_2$, prepared by converting $\alpha\zeta$-di-iodohexane, b. p. 151—155° (compare Hamonet, A., 1903, i, 306), into the corresponding diacetate and heating the latter with fuming hydrobromic acid in a sealed tube at 120°, forms a colourless liquid, b. p. 119·5—121°/18 mm.

Hexamethylene sulphide, $\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\ | \\ CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}\!>\!S$, obtained in small yield by the action of sodium sulphide on $\alpha\zeta$-dibromohexane in alcoholic solution, is a colourless, mobile liquid with the odour characteristic of cyclic sulphides, b. p. 169—171° (corr.)/747 mm., D_4^{18} 0·9743, n_D^{18} 1·5044. It forms a *methiodide*, $C_6H_{12}S,MeI$, which crystallises in long, colourless, oblique prisms, m. p. 137·5—138·5°, and a *compound* with mercuric chloride, $C_6H_{12}S,HgCl_2$, m. p. 149°. When oxidised with permanganate it gives the corresponding *sulphone*, $C_6H_{12}{:}SO_2$, which crystallises in long, colourless needles, m. p. 70·5—71°.

When $\alpha\kappa$-dibromodecane is heated with sodium sulphide in alcoholic solution in a sealed tube at 120—200°, very little action takes place, the formation of cyclic sulphide being detectable only by the odour of the products.

T. H. P.

Rupture of the Ring of Cyclic Sulphides. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 951—959).—When treated with alkali hydroxide, the methiodides of tertiary cyclic imines yield unsaturated open-chain amines,

$$\begin{matrix}CH_2{\cdot}CH_2\\ | \\ CH_2{\cdot}CH_2\end{matrix}\!>\!NMe_2I - HI = CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,$$

and diethylene disulphide methiodide undergoes a similar change:

$$S\!<\!\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}\!>\!SMeI - HI = CH_2{:}CH{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SMe.$$

The author has therefore investigated the action of alkali hydroxide on the methiodides of various cyclic sulphides which might

be expected to undergo conversion into unsaturated open-chain sulphides.

When heated with excess of 30% potassium hydroxide solution, 2-methyltetrahydrothiophen methiodide yields an unsaturated *sulphide*, $C_6H_{12}S$, which is a colourless, mobile liquid with a disagreeable odour, b. p. 144—146° (corr.)/748 mm., D_4^{18} 0·8934, n_D^{18} 1·4758. It combines with four atoms of bromine, giving a highly unstable compound, and yields a *methiodide*, $C_6H_{12}S,MeI$, crystallising in shining prisms, m. p. 68·5—70·5°. Oxidation of the unsaturated sulphide with permanganate yields acetic acid, a trace of formic acid, and a non-volatile, viscous liquid acid, the *sodium* salt of which, $C_4H_7O_4SNa$, was analysed. The conclusion is drawn that the sulphide has the structure $SMe\cdot CH_2\cdot CH_2\cdot CH:CHMe$, and that its formation is represented by the equations:

$$(1)\ \begin{matrix} CH_2\cdot CHMe \\ | \\ CH_2 — CH_2 \end{matrix}\!\!>\!SMe\cdot OH = OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot S\cdot CH_3,$$

and (2) this $-H_2O = SMe\cdot CH_2\cdot CH_2\cdot CH:CHMe$. The occurrence of a trace of formic acid among the oxidation products is probably due to the presence of a small proportion of the isomeric sulphide, $SMe\cdot CHMe\cdot CH_2\cdot CH:CH_2$.

Under similar conditions, pentamethylene sulphide methiodide is converted by the action of potassium hydroxide into the original pentamethylene sulphide, no unsaturated open-chain sulphide being obtained in this case.

The action of potassium hydroxide solution on 2-methylpentamethylene sulphide methiodide gives the unsaturated open-chain *sulphide*, $CHMe:CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot S\cdot CH_3$, which is a colourless liquid with an extremely disagreeable odour, b. p. 161—163° (corr.)/748 mm., 51·5—52°/15 mm., D_4^{18} 0·8985, n_D^{18} 1·4774, and yields a *methiodide*, $C_7H_{14}S,MeI$, which crystallises in colourless needles volatilising without melting at 157—158°. If the unsaturated sulphide and methyl iodide are heated in acetone solution in a sealed tube at 120°, trimethylsulphonium iodide results. Oxidation of the unsaturated sulphide by means of permanganate yields acetic acid.

A mechanism similar to that given above for the conversion of 2-methyltetrahydrothiophen methiodide into unsaturated sulphide is suggested for Hofmann's transformation of the methiodides of cyclic imines into unsaturated open-chain amines. T. H. P.

Behaviour of Dihalogenated Compounds towards Alkali Sulphides. General Characteristics of the Sulphides Formed. E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 959—974. Compare preceding abstracts).—The properties of cyclic sulphides are compared with those of cyclic compounds containing in the ring an oxygen atom, an imino-group, oxygen and carbonyl, imino- and carbonyl groups, etc. As regards the capacity for ring-closure and for reactions in which the ring is ruptured, cyclic sulphides have much in common with the cyclic oxides and imines containing rings of the same magnitude; the

analogies advanced by von Braun (A., 1911, i, 75) do not, therefore, correspond with the experimental data.

In most cases the action of sodium sulphide on dibromo-compounds leads to the formation of three products in varying relative proportions: the unimolecular sulphide, a product which contains sulphur and halogen and is probably a dihalogenated thio-ether, and a polymerised sulphide.

The cyclic sulphides obtained by the author by the action of sodium sulphide on dibromo-compounds contain from three to ten carbon atoms and rings with four to seven members. They are colourless, mobile liquids with unpleasant, characteristic odours, and they distil undecomposed and are readily volatile in a current of water-, alcohol-, or ether-vapour. They are insoluble in water, but mix in all proportions with ordinary organic solvents. Chemically, they are analogous to the aliphatic thio-ethers, and they are readily oxidised by permanganate to the corresponding sulphones and by dilute nitric acid to sulphoxides. With methyl iodide they form crystalline methiodides, and they combine readily with mercuric chloride and with bromine, the products in the latter case being very unstable; they do not react with benzoyl chloride, alkalis, or sodium.

With homologues derived from trimethylene, tetramethylene, and pentamethylene sulphides by replacement of one or two hydrogen atoms by methyl groups, each of the latter raises the boiling point by about 10°. The introduction of an extra methylene group into the ring raises the boiling point by about 26°. The boiling points of isomeric sulphides containing rings of different magnitudes vary very considerably. The specific gravities of homologues derived from cyclic sulphides by replacement of hydrogen atoms by methyl groups form a gradually diminishing series, whilst those of isomeric sulphides increase regularly as the magnitude of the ring increases.

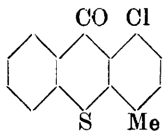
Calculation of the atomic refraction of sulphur by subtraction of the sum of the atomic refractions of the carbon and hydrogen atoms from the molecular refractions of the cyclic sulphides leads to values lying between 7·40 and 8·41, the mean being 7·84, which is very near to the value, namely, 7·65, of the atomic refraction of sulphur in compounds of the thiophen series. This result was scarcely to be expected in view of the fact that, with oxygen, nitrogen, etc., the magnitude of the atomic refraction varies within comparatively wide limits as the chemical function of the atom and the character of the compound change, and that whereas the sulphur atom is incapable of changing its valency in thiophen, in the cyclic sulphides it readily assumes quadri- or sexa-valency.

In cyclic sulphones, the atomic refraction of oxygen is calculated to have the mean value 0·45. T. H. P.

The Thioxanthone and Benzophenone-sulphone Series. F. Ullmann and Otto von Glenck (*Ber.*, 1916, **49**, 2487—2514).—The authors deemed it to be of interest to prepare thioxanthone derivatives with auxochromic groups adjacent

to the chromophoric carbonyl group, and have chosen as a convenient source of such compounds 1-chlorothioxanthones. These can be prepared readily by the condensation of chlorobenzenes with *o*-thiolbenzoic acid (Davis and Smiles, T., 1910, **97**, 1290).

When *o*-thiolbenzoic acid is condensed with *p*-chlorotoluene, it is possible that both 1-chloro-4-methyl- and 4-chloro-1-methylthioxanthones might be formed, only the former being of interest in this research:



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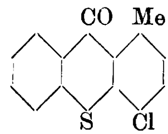
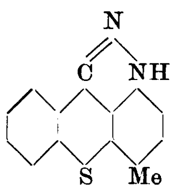


Both are formed, to the extent of 60% of the desired one and 40% of the other, as subsequent condensations show, but the mixture appears at first sight to be a perfectly homogeneous substance having a constant m. p., 148—148·5°. It is extremely difficult to separate these, but by taking advantage of the fact that the 1-chloro-compound is comparatively non-volatile at above 200° in a vacuum, whilst the 4-chloro-compound does not react any further with thiolbenzoic acid, the two individuals have been isolated. 1-*Chloro*-4-*methylthioxanthone* forms doubly refractive, colourless needles, m. p. 150—150·5°, and 4-*chloro*-1-*methylthioxanthone* has m. p. 142·5—143°. The latter has been synthesised as follows: 4-chloro-3-nitrotoluene is reduced to 4-chloro-*m*-toluidine by means of iron turnings and acetic acid; this is converted into 4-chloro-3-iodotoluene, b. p. 249°, which is then boiled with *o*-thiolbenzoic acid, potassium carbonate, and a trace of copper acetate in amyl alcohol. The 2-p-*chloro*-m-*tolylthiolbenzoic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_3MeCl,$$

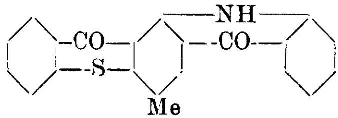
which is thus formed, in pearly needles, m. p. 193°, yields the desired 4-chloro-1-methylthioxanthone when dissolved in sulphuric acid monohydrate.

For the purpose of further condensations, the mixture of the isomerides is suitable, as the 4-chloro-compound is inactive. Thus, with hydrazine hydrate in alcohol, in the presence of a trace of cuprous chloride, at 180°, the *anhydride* of 4-*methylthioxanthonyl*-1-*hydrazine* (annexed formula) is produced in colourless spikes, m. p. 251°. With boiling aniline and potassium acetate and a trace of copper, 1-*anilino*-4-*methylthioxanthone* is formed in pale orange needles, m. p. 127°. Similarly, *p*-toluidine gives 1-p-*toluidino*-4-*methylthioxanthone*, reddish-orange needles, m. p. 132°, and *p*-toluenesulphonamide forms 1-p-*toluenesulphonylamino*-4-*methylthioxanthone*, in pale yellow, flat prisms, m. p. 191·5°. The last-named yields 1-*amino*-4-*methylthioxanthone* on hydrolysis with warm, concentrated sulphuric acid, in orange-yellow needles and prisms, m. p. 134°. The isomeric 4-*amino*-1-*methylthioxanthone* is obtained in canary-yellow prisms, m. p. 184°, by condensing *o*-thiolbenzoic acid with *p*-toluenesulpho-*p*-toluidide in



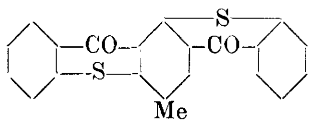
fuming sulphuric acid. Anthranilic acid condenses in boiling amyl alcohol to form 4-*methylthioxanthonyl*-1-*anthranilic acid*, orange-coloured, rhombic leaflets, m. p. 274°, which condenses still further in concentrated sulphuric acid to form 4-*methylthioxanthone*-2 : 1-*acridone*, thus:

$$C_6H_4{<}{\substack{CO\\ S}}{>}C_6H_2Me\cdot NH\cdot C_6H_4\cdot CO_2H \longrightarrow$$



The latter crystallises in pale yellow clusters of very slender needles, m. p. 297·5°. *o*-Thiolbenzoic acid yields o-4-*methylthioxanthonylthiolbenzoic acid* in yellow prisms, m. p. 248°, and this also condenses in sulphuric acid to give 4-*methyldithioxanthone*, in golden-yellow scales, m. p. 272·5°, thus:

$$C_6H_4{<}{\substack{CO\\ S}}{>}C_6H_2Me\cdot S\cdot C_6H_4\cdot CO_2H \longrightarrow$$

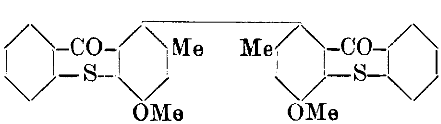


Finally, condensation between two molecules of 1-chloro-4-methylthioxanthone to 4 : 4′-*dimethyl*-1 : 1′-*dithioxanthonyl*,

$$C_6H_4{<}{\substack{CO\\ S}}{>}C_6H_2Me\cdot C_6H_2Me{<}{\substack{CO\\ S}}{>}C_6H_4.$$

takes place when the substance is boiled with naphthalene and copper powder. This crystallises in pale yellow, flat prisms, m. p. 332°.

6-Chloro-*m*-methoxytoluene condenses more readily with *o*-thiolbenzoic acid than *p*-chlorotoluene does, and yields exclusively 1-*chloro*-4-*methoxy*-2-*methylthioxanthone*, in pale yellow prisms or slender needles, m. p. 185°. Further condensations were effected with this compound in order to determine the influence of the methoxy-group on the colour. 4-*Methoxy*-2-*methylthioxanthonyl*-1-*anthranilic acid* crystallises in slender, orange needles, m. p. 285°. 1-*Anilino*-4-*methoxy*-2-*methylthioxanthone* forms long, yellow needles from acetic acid, or rhombic leaflets from alcohol, m. p. 183°. 1-p-*Toluenesulphonylamino*-4-*methoxy*-2-*methylthioxanthone*, yellow prisms, m. p. 188°, yields 1-*amino*-4-*methoxy*-2-*methylthioxanthone*, brick-red needles, m. p. 144°, on hydrolysis. 4 : 4′-*Dimethoxy*-2 : 2′-*dimethyl*-1 : 1′-*dithioxanthonyl* (annexed formula) is obtained by boiling the chloro-compound with naphthalene and copper powder, in pale yellow, slender needles, m. p. 372°, a small amount of

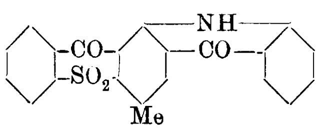


4-*methoxy*-2-*methylthioxanthone*, m. p. 167—168°, being formed at the same time.

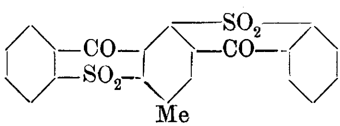
Several of these thioxanthones have been oxidised to benzophenonesulphones by means of 30% hydrogen peroxide in glacial acetic acid or potassium persulphate in concentrated sulphuric acid. 1-*Chloro*-4-*methylbenzophenonesulphone*,

$$C_6H_4<{CO \atop SO_2}>C_6H_2MeCl,$$

crystallises in colourless prisms or tablets, m. p. 184—185° (the 4-chloro-1-methyl isomeride must also be contained in this), and condenses with anthranilic acid to form 1-*anthranilo*-4-*methylbenzophenonesulphone*, in orange-red needles or prisms, m. p. 317°. This condenses further in concentrated sulphuric acid to 4-*methylbenzophenonesulphone*-2 : 1-*acridone* (annexed formula), which



crystallises in pale ruby-red, glistening needles, m. p. 303°. 1-*Chloro*-4-*methoxy*-2-*methylbenzophenonesulphone* forms pale yellow needles, m. p. 183°. 1-*Anilino*-4-*methoxy*-2-*methylbenzophenonesulphone* crystallises in garnet-red prisms, m. p. 192—193°, and the corresponding 1-p-*toluidino*-compound in ruby-red cubes, m. p. 184°. 4-*Methyldibenzophenonedisulphone* (annexed



formula), the product of the oxidation of 4-methyldithioxanthone, forms almost colourless needles, m. p. 328°.

All the melting points are "corrected." J. C. W.

[*iso*-**Nortropinone**]. J. Houben and Alexander Pfau (*Ber.*, 1916, **49**, 2745. Compare this vol., i, 25).—A compound referred to in the discussion was designated "nortropinone." It should have been *iso*nortropinone. J. C. W.

Degradation of Scopoline. K. Hess (*Ber.*, 1916, **49**, 2745. Compare this vol., i, 52).—A question of priority. J. C. W.

Rupture of the Ring [Nitrogen] in Hydrohydrastinine and Hydrocotarnine by means of Cyanogen Bromide. J. von Braun (*Ber.*, 1916, **49**, 2624—2629).—When 2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline is treated with cyanogen bromide, the elements of this agent are attached at the 1 and 2 positions, and the ring is ruptured. Although the *o*-β-cyanomethylamino-ethylbenzyl bromide which is thus formed has not been purified, it seemed worth while to apply the same reaction to alkaloids of the same type, particularly as the nitrogen ring is thereby opened at a point other than that affected in the Hofmann degradation.

Hydrohydrastinine, when treated with cyanogen bromide in

ether, yields the expected product, 2-*β-cyanomethylaminoethyl*-4:5-*methylenedioxybenzyl bromide*,

$$CH_2{:}O_2{:}C_6H_2(CH_2Br){\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}CN,$$

as a snow-white mass, m. p. 109°, which is not very stable, especially in the light and in contact with hydroxylic solvents. As an active bromide, it readily reacts with piperidine to form the *compound*, $C_{11}H_{11}O_2N_2{\cdot}CH_2{\cdot}C_5H_{10}N$, m. p. 155°, and with pyridine to form the *quaternary bromide*, $C_{11}H_{11}O_2N_2{\cdot}CH_2{\cdot}C_5H_5NBr$, m. p. 209°. A similar *quaternary bromide* of hydrohydrastinine, m. p. 165°, accompanies the bromide in the introductory reaction.

Hydrocotarnine gives an even more reactive product, 2-*β-cyanomethylaminoethyl*-6-*methoxy*-4 : 5-*methylenedioxybenzyl bromide*, m. p. 74°, which readily polymerises to a glassy mass when warmed on the water-bath. J. C. W.

Insoluble Morphine in Crude Opium. P. CARLES (*J. Pharm. Chim.*, 1917, [vii], **15**, 44—47).—The author has not been able to obtain any evidence of the presence of an insoluble modification of morphine in crude opium. Statements by various observers that such a modification exists are possibly due to the fact that large masses of opium are not readily penetrated by water or dilute alcohol, and that small quantities of solvent fail to extract the whole of the morphine. W. P. S.

The Morphine Alkaloids. IV. J. VON BRAUN and K. KINDLER (*Ber.*, 1916, **49**, 2655—2663. Compare A., 1914, i, 1138; 1916, i, 500, 665).—It was shown in the case of aminocyanonorcodeine that the physiological activity of codeine, which is lost by removing the basic properties of the ring-nitrogen, is not restored by the introduction of an amino-group in the aromatic nucleus. The effect of the transposition of a hydroxyl group is found to be practically the same; although the group is still present in another part of the molecule, the physiological activity is greatly lessened. Furthermore, the properties of codeine cannot be reproduced by building up a simpler molecule containing the various "groups" of codeine, that is, a methoxylated benzene ring, a nitrogen ring with methylated nitrogen, and an alcohol group. It appears that the deciding factor in the case of codeine and morphine is the position of the nitrogen with regard to the bridged hexamethylene ring (A., 1914, i, 1138).

Although the $>N{\cdot}[CH_2]_3{\cdot}OBz$ grouping is associated with many anæsthetics, it is found that in norcodeine it has no such influence.

Cyanonormorphine reacts with *p*-nitrobenzyl chloride in the presence of sodium ethoxide to form p-*nitrobenzylcyanonormorphine*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}C_{16}H_{14}O(OH){:}N{\cdot}CN$, m. p. 229°, which may be hydrolysed to p-*nitrobenzylnormorphine*, pale yellow crystals, m. p. 180° (*hydrochloride*, decomp. 297°), or converted into p-*aminobenzylcarbamidonormorphine*,

$$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}C_{16}H_{14}O(OH){:}N{\cdot}CO{\cdot}NH_2,$$

colourless leaflets, m. p. 297°, by warming with stannous chloride and hydrochloric acid.

Norcodeine reacts readily with *op*-dinitrobromobenzene to form

op-*dinitrophenylnorcodeine*, deep yellow, m. p. 265°, which is easily reduced to op-*diaminophenylnorcodeine*,

$$OH\cdot C_{16}H_{14}O(OMe)\colon N\cdot C_6H_3(NH_2)_2,$$

m. p. 233°. This forms an *acetyl* compound, m. p. 144—146°, which reacts readily with cyanogen bromide, suffering rupture of the nitrogen ring, and giving an unsaturated *cyanamide*, $C_{30}H_{30}O_6N_4$, m. p. 148—149°, and this compound may be hydrolysed to an unsaturated *base*,

$$OH\cdot C_{16}H_{13}O(OMe)\cdot N(CN)\cdot C_6H_3(NH_2)_2,$$

m. p. 168—169°. *p*-Bromonitrobenzene reacts with norcodeine very sluggishly, giving p-*nitrophenylnorcodeine*, m. p. 212°.

α-Chlorocyanonorcodide reacts with dimethylamine to form *dimethylaminocyanonorcodide*, $NMe_2\cdot C_{16}H_{14}O(OMe)\colon N\cdot CN$, m. p. 192° (*hydrochloride*, m. p. 266°; *picrate*, m. p. 190°; *methiodide*, m. p. 203°), and this may be hydrolysed to *dimethylaminonorcodide*, m. p. 128° (*picrate*, m. p. 218°; *platinichloride*, m. p. 275—276°). For comparison with this, α-chlorocodide was converted into *dimethylaminocodide*, $NMe_2\cdot C_{16}H_{14}O(OMe)\colon NMe$, m. p. 118° (*platinichloride*, m. p. 250°), and *diethylaminocodide*, m. p. 102° (*platinichloride*, decomp. 240°). Dimethylaminonorcodide unites with ethylene oxide to form *dimethylamino*-N-*β-hydroxyethylnorcodide*, $OH\cdot C_2H_4\cdot N\colon C_{16}H_{14}O(OMe)\cdot NMe_2$, as a very hygroscopic substance, m. p. 85°, which yields a yellow *platinichloride*, m. p. 255°.

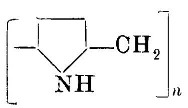
Methylthalline (6-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline) is best separated from the product of the action of methyl iodide on thalline by benzoylating, and extracting the unaffected tertiary base by sulphuric acid. It has b. p. 150—151°/10 mm., forms a *picrate*, leaflets, m. p. 164°, and combines with formaldehyde to give 6-*methoxy*-8-*hydroxymethyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, $OH\cdot CH_2\cdot C_6H_2(OMe){<}\begin{matrix}CH_2\text{—}CH_2\\ NMe\cdot CH_2\end{matrix}$, as a yellow, viscous oil, b. p. 203—207°/10 mm.

Norcodeine reacts with γ-bromopropyl benzoate (A., 1913, i, 720) under the conditions for the alkylation of norcodeine recently devised (A., 1916, i, 665) to form *γ-benzoyloxypropylnorcodeine*, $OH\cdot C_{16}H_{14}O(OMe)\colon N\cdot C_3H_6\cdot OBz$, m. p. 47°. This yields a hydrochloride, a *picrate*, m. p. 118—119°, and a *methiodide*, m. p. 169—170°, and may be hydrolysed easily to *γ-hydroxypropylnorcodeine*, m. p. 133° (*picrate*, yellow leaflets, m. p. 120—121°).

J. C. W.

Condensation of Pyrrole and 1-Methylpyrrole with Formaldehyde: Preparation of Glycols of the Pyrrole Series. V. V. TSCHELINCEV and B. V. MAKSOROV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 748—779).—The condensation of pyrrole with formaldehyde in presence of an acid (compare Pictet and Rilliet, A., 1907, i, 445) yields a non-oxygenated product containing one formaldehyde residue to one pyrrole residue. The results of experiments on the condensation of pyrrole with acetone (Tschelincev and Tronov, this vol., i, 91, 93) and of those described below indicate

that the structure of the above compound is represented by the annexed formula. Treatment of this compound with hydrochloric acid in acetone yields a cinnabar-coloured, amorphous substance, which is turned yellow by potassium hydroxide, and gives analytical results corresponding approximately with the formula $C_{30}H_{36}O_3N_4$. By hydrochloric acid in ethyl-alcoholic solution, the same product is converted into an orange-yellow, gelatinous substance of the composition $C_{28}H_{34}O_6N_4$. Owing to their slight solubility and ready alteration, these products were not further investigated.



The above product, $(C_5H_5N)_n$, is also obtained by the condensation of pyrrole (1 mol.) and 4% formaldehyde solution (1 mol.) in absence of acid at the ordinary temperature. When, however, under these conditions 20% formaldehyde solution is employed, the result of the condensation is an almost colourless substance which has the composition $C_{27}H_{30}O_3N_4$ and the molecular weight 505 in freezing bromoform, the calculated value being 458. This substance differs from those obtained in presence of an acid by its ready solubility in most solvents; when treated with hydrochloric or sulphuric acid, it is converted into a bright yellow, amorphous, flocculent substance similar to those described above.

More definite results are obtained when the condensation is carried out in presence of potassium carbonate at 80—90°. Under these conditions, pyrrole and formaldehyde yield the glycol, 2:5-*dimethylolpyrrole*, $\begin{matrix}CH{:}C(CH_2{\cdot}OH)\\ |\\ CH{:}C(CH_2{\cdot}OH)\end{matrix}\!>\!NH$, which forms long, colourless needles, m. p. 117—118°, exhibits normal cryoscopic behaviour in water, and by inorganic or organic acids is converted into an orange-yellow, voluminous, flocculent substance, $C_{18}H_{22}O_5N_2$. When oxidised with silver oxide, this glycol gives pyrrole-2:5-dicarboxylic acid, which was identified by means of its methyl ester and by the methyl ester of its 3:4-dibromo-derivative (compare Ciamician and Silber, A., 1886, 938).

The glycol, 1-*methyl*-2:5-*dimethylolpyrrole*,

$$\begin{matrix}CH{:}C(CH_2{\cdot}OH)\\ |\\ CH{:}C(CH_2{\cdot}OH)\end{matrix}\!>\!NMe,$$

obtained by condensation of 1-methylpyrrole and formaldehyde in presence of potassium carbonate, forms spherical, drusy masses of white needles, m. p. 113—114°, exhibits normal cryoscopic behaviour in water, and is converted into an insoluble, orange, gelatinous, flocculent substance, $C_{19}H_{16}O_3N$, by the action of acids. On oxidation with sodium peroxide and permanganate, the glycol yields 1-methylpyrrole-2:5-dicarboxylic acid (compare Fischer, A., 1913, i, 1225); the *methyl* ester of this acid, $C_9H_{11}O_4N$, m. p. 80—81°, and *methyl* 3:4-*dibromo*-1-*methylpyrrole*-2:5-*dicarboxylate*, $C_9H_9O_4NBr_2$, m. p. 159°, were prepared. T. H. P.

New Method of Preparing Pyrrole-2 : 5-dicarboxylic Acids. V. V. Tschelincev and B. V. Maksorov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 779—790).—These acids may be obtained in good

yields by oxidation of the corresponding glycols, which are themselves readily obtainable by the condensation of pyrroles with formaldehyde in presence of potassium carbonate (compare preceding abstract). T. H. P.

Inactivity of the γ-Carbonyl of certain Pyrone and Pyridone Derivatives. IV. SCHÖTTLE (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 530—532).—The inactivity of the γ-carbonyl of pyrones towards hydroxylamine and phenylhydrazine has been established by a number of investigations. In most cases, these reagents either do not react or else replace the oxygen of the nucleus. The author now finds that similar inactivity towards these two reagents is exhibited by the γ-carbonyl group in 2:6-diphenylpyridone, 4-hydroxypyridine-2:6-dicarboxylic acid, 4-hydroxy-1-methylpyridine-2:6-dicarboxylic acid, 1-phenoxypyridone, and 1-phenylpyridone, the unaltered compound being recoverable in all cases.

According to these results, in the reaction between hydroxylamine or phenylhydrazine with lactamic derivatives of benzoyldehydracetic acid (A., 1915, i, 695), there is no possibility of the formation of oxime or phenylhydrazone at the γ-carbonyl group. If such reaction were to take place, the formation of a compound of the type $O\Big<\begin{matrix}CPh{:}C\cdot CO{-}N\cdot OH\\ N{=\!=}C\cdot CH{:}CPh\end{matrix}$ would be expected, and this, when heated with concentrated hydrochloric acid and subsequently oxidised, should undergo decompositions, resulting in the formation of 5-phenyl*iso*oxazole-3-carboxylic acid, m. p. 162°:

$$\rightarrow O\Big<\begin{matrix}CPh{:}C\cdot CO_2H\\ N{=\!=}C\cdot CH{:}CPh\cdot NH\cdot OH\end{matrix} \rightarrow$$

$$O\Big<\begin{matrix}CPh{:}CH\\ N{=\!=}C\cdot CH_2\cdot COPh\end{matrix} \rightarrow O\Big<\begin{matrix}CPh{:}CH\\ N{=\!=}C\cdot CO_2H\end{matrix}.$$

The acid actually obtained by the author under these conditions has, however, m. p. 177—178°, and, when distilled, does not yield 5-phenyl*iso*oxazole or cyanoacetophenone. Support is thus afforded to the formulation of the reaction previously given by the author (*loc. cit.*). T. H. P.

Auto-oxidation of Indoles in Daylight. OSKAR BAUDISCH and ARTHUR BARON HOSCHEK (*Ber.*, 1916, **49**, 2579—2583).—When suspensions of 2-methylindole in water are exposed to the light in the presence of oxygen, the solid and liquid become very dark brown in time, and the gas is absorbed. Some details of the examination of products obtained in this way in the bright sunlight of the Alps are given. It appears that the first product is a red, amorphous polymeride, which then suffers partial photolysis and oxidation to *di-2-methyl-3-indolyl ether*,

$$O\left(C\Big<\begin{matrix}C_6H_4\\ CMe\end{matrix}\Big>NH\right)_2$$

which forms long, sulphur-yellow, rhombic crystals, m. p. 210°. This ether then undergoes further hydrolysis and oxidation to

N-acetylanthranilic acid and anthranilic acid itself. The two stages in the oxidation can be realised also by boiling the red powder with alkaline permanganate.

Indole seems to behave in a similar manner, which is significant in view of the fact that methyl anthranilate and indole are known to occur together in some plants, for example, in *Robinia pseudo-acacia*, L. J. C. W.

Condensation of Indoles with Aromatic Aldehydes. ARTHUR BARON HOSCHEK (*Ber.*, 1916, **49**, 2584—2588).—In the course of some experiments on the auto-oxidation of 2-methylindole (preceding abstract), it seemed possible at first that *o*-acetylaminobenzaldehyde might be formed and then condense with the unchanged base. Condensations of *o*-aminobenzaldehyde with indole and 2-methylindole, and of *o*-acetylaminobenzaldehyde with the latter base, have therefore been effected by heating the substances together in sealed tubes. No reaction seems to take place at lower temperatures, but normal benzylidene compounds are formed at about 140—160°.

3 : 3′-o-*Aminobenzylidenedi-indole* (*di-3-indolyl-*o*-aminophenylmethane*), $NH_2\cdot C_6H_4\cdot CH\left(C{\lessdot}^{\overline{\quad\quad\quad}}_{CH\cdot NH}{\gtrdot}C_6H_4\right)_2$, forms pale yellow leaflets, m. p. 97°, and yields a brick-red *hydrochloride*, m. p. 244°. 3 : 3′-o-*Aminobenzylidenedi-2-methylindole* is a snow-white powder, m. p. 250°, and its *hydrochloride*, 3HCl, forms pearly needles and leaflets. 3 : 3′-o-*Acetylaminobenzylidenedi-2-methylindole* is a white substance, m. p. 210°, which becomes red in contact with traces of acids. J. C. W.

Scission of the Hydrogenated Indole and Quinoline Rings by Reduction. III. Substituted Hydroindole Bases. J. VON BRAUN, K. HEIDER, and L. NEUMANN (*Ber.*, 1916, **49**, 2613—2624. Compare A., 1916, i, 421, 742).—It was recently shown that when the quaternary methochloride of dihydroindole is treated with sodium amalgam, it is reduced to 1-methyldihydroindole, β-dimethylaminoethylbenzene, and *o*-dimethylaminoethylbenzene concurrently. Some dihydroindoles, loaded with side-chains in the pyrrole ring, have now been examined under the same conditions in order to test the influence of substituents on the reduction. The results tabulated below show how great the influence is, especially on the yield of the ortho-substituted dimethylaniline. Such a difference in the stability of the indole ring is not apparent in the case of the Hofmann reaction.

	Tertiary cyclic base.	Substituted dimethyl-aniline.	Aryl-aliphatic amine.
2 : 3-Dihydroindole	75%	8%	17%
2-Methyl-2 : 3-dihydroindole	40	40	20
3-Methyl-2 : 3-dihydroindole	76	trace	24
2 : 3 : 3-Trimethyl-2 : 3-dihydroindole	90	10	trace
Hexahydrocarbazole	88	3·6	8·4

The methochloride of dihydromethylketole (1:1:2-trimethyl-2:3-dihydroindolium chloride) yields: (1) 1:2-dimethyl-2:3-dihydroindole, which is isolated as the di-indylmethane *compound*, $CH_2\left(C_6H_3<{CH_2-\atop NMe}>CHMe\right)_2$, m. p. 120°; (2) *o-dimethylaminopropylbenzene*, b. p. 104—105°/17 mm., which forms a *picrate*, m. p. 150°, a *platinichloride*, m. p. 146°, and a *methiodide*, m. p. 148°; (3) β-dimethylaminopropylbenzene, which is obtained in the form of the *methiodide*, $CH_2Ph\cdot CHMe\cdot NMe_3I$, m. p. 228°, and identified by conversion into trimethylamine and the known *iso*allylbenzene, CHPh:CHMe, in the usual way.

Dihydroscatole is converted into the methiodide, 1:1:3-*trimethyl-2:3-dihydroindolium iodide*, m. p. 203—204°, and, after treating this with silver chloride, sodium amalgam, and formaldehyde, and separating the solid methylene compound, a trace of *o*-dimethylamino*iso*propylbenzene (*picrate*, m. p. 139°) and also *β-dimethylamino*iso*propylbenzene*, $CHPhMe\cdot CH_2\cdot NMe_2$, b. p. 97—98°/18 mm., are found in the volatile products. The latter forms a *methiodide*, m. p. 158°, which yields trimethylamine and α-methylstyrene, CPhMe:CH$_2$, b. p. 163—164°/752 mm., when the corresponding hydroxide is distilled.

2:3:3-Trimethyl-2:3-dihydroindole has furnished the following new compounds: the methylene *compound* of the methiodide of the *tert.*-base, $CH_2\left(C_6H_3<{CMe_2-\atop NMe_2I}>CHMe\right)_2$, m. p. above 300° (decomp.), and almost pure *o-dimethylamino*iso*amylbenzene*, b. p. 122—123°/23 mm., which forms a *hydrochloride*, m. p. 164°, and a *picrate*, yellow needles, m. p. 182°.

Hexahydrocarbazole (Borsche, A., 1908, i, 365) forms a quaternary *methiodide*, $C_{14}H_{20}NI$, m. p. 187°, which may be converted into 1-*methylhexahydrocarbazole*, b. p. 162°/24 mm., in the usual way, but it is believed that during the distillation a small portion of the substance suffers rupture of the *N*-ring, giving an impurity which makes the constants for the expected base and its salts indefinite. The base condenses with formaldehyde to yield the *compound*, $CH_2\left(C_6H_3<{C_6H_{10}\atop NMe}\right)_2$, m. p. 116—117°, which forms a *hydrochloride*, m. p. 110°, and a *methiodide*, m. p. 180°. When the methiodide is treated with silver chloride, sodium amalgam, and formaldehyde, the same methylene compound is obtained in a high yield, and from the volatile bases can be separated *o-dimethylaminophenyl*cyclo*hexane*, which is characterised by a *platinichloride*, m. p. 169—170°, a *picrate*, m. p. 160°, and also the *methiodide*, $C_6H_5\cdot C_6H_{10}\cdot NMe_3I$, m. p. 119°. When the ammonium hydroxide corresponding with this is distilled, the main product is 2:3:4:5-tetrahydrodiphenyl (1-phenyl-Δ^1-*cyclo*hexene), b. p. 132°/26 mm., D_4^{20} 0·9931, n_D^{20} 1·57179 (compare Auwers and Treppmann, A., 1915, i, 789), mixed with some *o*-dimethylaminophenyl*cyclo*hexane (*o*-phenyl*cyclo*hexyldimethylamine), $C_6H_{10}Ph\cdot NMe_2$, which is characterised by a *picrate*, m. p. 164—165°. J. C. W.

The Relative Stability of the Rings in Cyclic Bases under the Conditions of the Hofmann Reaction. J. VON BRAUN (*Ber.*, 1916, **49**, 2629—2642).—Researches during recent years on the action of cyanogen bromide on cyclic compounds containing nitrogen have shown that the resistance offered to the disruption of the ring increases in the order: dihydro*iso*indole and tetrahydro*iso*quinoline, pyrrolidine, piperidine, and tetrahydroquinoline. It seemed to be of interest, therefore, to devise a scheme by which the stability of these ring systems during the Hofmann reaction could be tested, and salts like the "pyrrolidylpiperidinium" bromide recently described (A., 1916, i, 632) offer the way. The hydroxides of four such compounds have been heated, and the weaker of the two rings determined by an examination of the products. It is found, again, that the stability of the ring increases in the order: tetrahydro*iso*quinoline, dihydro*iso*indole, pyrrolidine, piperidine, and dihydroindole and tetrahydroquinoline. This is remarkable, as the two reactions are so different, and it suggests that the stability of the ring is in some way intimately connected with the exercise of all the forces in the molecule as a whole.

The Hofmann reaction is usually defined as the production of an unsaturated, tertiary, open-chain base from a cyclic, quaternary ammonium hydroxide by the elimination of water, but the present experiments show that the loss of water is a secondary consideration. Hydroxy-amines are frequently formed.

Tetrahydro*iso*quinoline is warmed with $\alpha\epsilon$-dibromo(or di-iodo)-pentane and aqueous sodium hydroxide, and so converted into "*piperidyltetrahydro*iso*quinolinium hydroxide*" (annexed formula),

$$C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot \underset{\displaystyle OH}{\overset{|}{N}}:C_5H_{10}\end{matrix}$$

which forms an *iodide*, stout crystals, m. p. 147°, a *bromide*, m. p. 188°, and a *platinichloride*, m. p. 246°, and yields 1-o-*vinylbenzylpiperidine*,

$$CH_2:CH\cdot C_6H_4\cdot CH_2\cdot C_5H_{10}N,$$

on distillation under reduced pressure. This base has b. p. 151—152°/16 mm., and forms a *hydrochloride*, m. p. 205°, a *platinichloride*, an *aurichloride*, yellow leaflets, m. p. 108°, a *picrate*, m. p. 150°, and a *methiodide*, m. p. 161°. The constitution of the base is determined by its reaction with cyanogen bromide. This gives an oil with an odour like benzyl bromide, consisting of equivalent quantities of 1-cyanopiperidine, b. p. 105°/10 mm., and *o*-vinylbenzyl bromide, which are separated by the addition of trimethylamine, whereby the *methobromide* of o-*vinylbenzyldimethylamine*, m. p. 215°, is precipitated (compare Emde, A., 1912, i, 801), thus: $CH_2:CH\cdot C_6H_4\cdot CH_2\cdot C_5H_{10}N + BrCN = CH_2:CH\cdot C_6H_4\cdot CH_2Br + CN\cdot C_5H_{10}N$.

From $\alpha\delta$-dibromobutane, "*pyrrolidyltetrahydro*iso*quinolinium*" *bromide*, m. p. 168°, can be prepared, and the corresponding hydroxide converted into 1-o-*vinylbenzylpyrrolidine* by distillation. This base has b. p. 147—148°/21 mm., and forms a *picrate*, m. p. 110—111°, a *platinichloride*, leaflets, m. p. 155°, and a *methiodide*, m. p. 129°. Its constitution is again determined by the action of cyanogen bromide, which produces 1-cyanopyrrolidine, *o*-vinyl-

benzyl bromide, and a *quaternary bromide*, $C_{22}H_{26}NBr$, m. p. 100°, compounded of the latter and undecomposed *o*-vinylbenzylpyrrolidine.

o-Xylylene dibromide gives rise to "*dihydro*iso*indolyltetrahydroisoquinolinium*" *bromide*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot NBr\end{matrix}<\begin{matrix}CH_2\\ CH_2\end{matrix}>C_6H_4$, m. p. 210°, and the corresponding hydroxide mainly yields N-o-*vinylbenzyldihydro*iso*indole* on heating, as an oil which suffers partial decomposition on redistillation; b. p. 217—218°/18 mm., m. p. 41°; *hydrochloride*, m. p. 177°; *picrate*, m. p. 121°; *methiodide*, m. p. 175°.

The action of heat on *o*-xylylenepiperidinium hydroxide ["dihydro*iso*indolylpiperidinium" hydroxide] was investigated by Scholtz and Wolfrum (A., 1910, i, 773). It is now suggested that the primary product is o-*piperidylmethylbenzyl alcohol*,

$$OH\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot C_5H_{10}N,$$

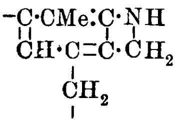
which has m. p. 71°, b. p. 181—182°/17 mm. The crude distillate, b. p. 190—210° (chiefly), 210—300°, deposits this solid, and the remaining oil possibly contains Scholtz's amylenyldihydro*iso*indole, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot C_3H_6\cdot CH:CH_2$, in the more volatile portions, but the less volatile oils are certainly decomposition products of the amino-alcohol. The latter forms a *hydrochloride*, m. p. 169—170°, a *platinichloride*, m. p. 197°, an *aurichloride*, m. p. 103°, a *picrate*, m. p. 140°, a *methiodide*, m. p. 135°, an *acetate*, m. p. 242°, the *picrate* of a *benzoate*, m. p. 120°, and the *platinichloride* of an *anisate*, m. p. 188°. The amino-alcohol also changes into the hydrochloride of the corresponding derivative of benzyl chloride when heated with hydrochloric acid, and the free chloro-base changes quickly into *o*-xylylenepiperidinium chloride on warming.

"*Dihydro*iso*indolylpyrrolidinium*" *bromide*, m. p. 165—166°, is prepared in the same way. The hydroxide did not yield a solid product on heating, but it was obvious that the pyrrolidine ring had not suffered much disruption.

"Piperidylpyrrolidinium" hydroxide (*loc. cit.*), when distilled, yields 1-δ-hydroxybutylpiperidine, b. p. 133—134°/20 mm. (*ibid.*), and a somewhat larger quantity of a fraction, b. p. 176—180°/atmos., which consists of a mixture of 1-Δ^{γ}-butenylpiperidine and 1-Δ^{δ}-pentenylpyrrolidine. This mixture was hydrogenated, and then, by careful fractionation, 1-*amylpyrrolidine*, b. p. 179°, was isolated. This base was also synthesised by the action of $\alpha\delta$-dibromobutane on *n*-amylamine. It forms a *picrate*, reddish-yellow needles, m. p. 118—119°, and a hygroscopic *methiodide*, m. p. 169—170°. J. C. W.

Condensation of Amines with Formaldehyde. P. M. KRONEBERG (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 305—309).—Investigation of the condensation of *o*-toluidine with formaldehyde in presence of dilute (1:6) sulphuric acid (compare Nastukov and Malkaln, A., 1912, i, 962; Nastukov and Kroneberg, *ibid.*) shows

that the melting point of the product varies with the temperature at which the reaction takes place. The *base* obtained in the cold has m. p. 183—185°, gives the molecular weight 1043 in freezing nitrobenzene, and on dry distillation yields *o*-toluidine, *m*-as.-xylidine, and diaminoditolylmethane. The base is formed according to the equation $(C_7H_9N + 2CH_2O)_8 = (2H_2O + C_9H_9N)_8$, and may be regarded as a polymeric form of the residue (annexed formula). When the condensation takes place at 65—70°, the product melts at 115—116° (112—113°), and when the reacting mixture is boiled, the resultant melting point is 110—111°. Further, all these products undergo a gradual fall in melting point on keeping, the melting point 183—183·5° changing to 103—104°. The melting points of the products given by formaldehyde and other bases in presence of dilute sulphuric acid in a boiling solution are: *m*-toluidine, 169—170°; xylidine, 58·5—59·5°; and *o*-anisidine, 133—134°.



It is evident that the molecular weight of the product given by such a condensation is a function of the temperature of the reaction, and that, at temperatures below the boiling point of the solution, the base obtained is unstable and undergoes molecular change in the air. The instability of the base obtained at the ordinary temperature is shown by the fact that its molecular weight is 129 in boiling pyridine (*loc. cit.*) and 1043 in freezing nitrobenzene. The products of the condensation of formaldehyde with other bases are being investigated. T. H. P.

Rhodanines, Parabanic Acids, and Related Substances. Karl H. Stieger (*Monatsh.*, 1916, **37**, 635—658).—An extension of the earlier investigations (Andreasch, A., 1910, i, 694; 1908, i, 683; 1907, i, 233, etc.).

3-*iso*Amylrhodanine, $\begin{matrix}S\text{—}CS\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot CH_2\cdot CH_2\cdot CHMe_2$, obtained by mixing *iso*amylamine, potassium hydroxide solution, and carbon disulphide, and treating the resulting solution of potassium *iso*amyldithiocarbamate with ethyl chloroacetate, is a viscous, yellow oil, b. p. 200°/14 mm., of faint odour. The following condensation products were prepared by heating equivalent quantities of the constituents with acetic acid for about an hour: 5-*benzylidene* derivative, $\begin{matrix}CS\text{———}S\\ N(C_5H_{11})\cdot CO\end{matrix}\!\!>\!C{:}CHPh$, bright yellow needles, m. p. 105°; 5-o-*hydroxybenzylidene* derivative, $C_{15}H_{17}O_2NS_2$, deep chrome-yellow needles, m. p. 175°; 5-p-*hydroxybenzylidene* derivative, deep yellow needles, m. p. 161°; 5-p-*methoxybenzylidene* derivative, $C_{16}H_{19}O_2NS_2$, pale chrome-yellow, prismatic needles, m. p. 116°; 5-p-*nitrobenzylidene* derivative, $C_{15}H_{16}O_3N_2S_2$, yellow, rhombic tablets, m. p. 163°; 5-p-*dimethylaminobenzylidene* derivative, carmine-red, crystalline scales, m. p. 154°; 5-mp-*methylenedioxybenzylidene* derivative, $C_{16}H_{17}O_3NS_2$, yellow needles, m. p. 111°.

*iso*Amylthiocarbamide, when treated in alcoholic solution with cyanogen, is converted into the *imide* of *iso*amylthioparabanic acid, $CS<\begin{matrix} N(C_5H_{11})\cdot C{:}NH \\ NH\text{———}C{:}NH \end{matrix}$, which, by warming with hydrochloric acid, is hydrolysed to iso*amylthioparabanic acid*, $\begin{matrix} NH\cdot CS \\ CO\cdot CO \end{matrix}>N\cdot C_5H_{11}$, yellow, silky needles, m. p. 125°; this on desulphurisation with silver nitrate in aqueous-alcoholic solution, yielded iso*amylparabanic acid*, $\begin{matrix} NH\cdot CO \\ CO\cdot CO \end{matrix}>N\cdot C_5H_{11}$, colourless, silky needles, m. p. 106°.

In a similar manner, phenyl*iso*amylthiocarbamide, on treatment with cyanogen and subsequent hydrolysis, yielded *phenyl*iso*amylthioparabanic acid*, $\begin{matrix} NPh\cdot CS \\ CO\text{—}CO \end{matrix}>N\cdot C_5H_{11}$, fine, pale yellow needles, m. p. 94°, which when desulphurised gave *phenyl*iso*amylparabanic acid*, $\begin{matrix} NPh\cdot CO \\ CO\text{—}CO \end{matrix}>N\cdot C_5H_{11}$, fine, colourless needles, m. p. 85°.

*Di*iso*amylthioparabanic acid*, $\begin{matrix} CO\cdot N(C_5H_{11}) \\ CO\cdot N(C_5H_{11}) \end{matrix}>CS$, prepared by hydrolysis of the additive compound of di*iso*amylthiocarbamide and cyanogen, was converted by desulphurisation in the general manner, with formation of *di*iso*amylparabanic acid*,

$$\begin{matrix} CO\cdot N(C_5H_{11}) \\ CO\cdot N(C_5H_{11}) \end{matrix}>CO,$$

both products being obtained as uncrystallisable syrups.

Di-p-*hydroxyphenylthioparabanic acid*, obtained by using di-*p*-hydroxyphenylthiocarbamide as starting point, formed yellow needles, which began to decompose near 360° without fusion, and on desulphurisation yielded colourless needles, m. p. above 360°.

p-*Tolyl*iso*amylthiocarbamide*, $C_5H_{11}\cdot NH\cdot CS\cdot NH\cdot C_6H_4Me$, needles, m. p. 217° (decomp.), was obtained by the action of *p*-toluidine on *iso*amylthiocarbimide in alcoholic solution; by the usual series of chemical changes it was converted into p-*tolyl*iso*amylthioparabanic acid*, $\begin{matrix} CO\text{——}N(C_5H_{11}) \\ CO\cdot N(C_6H_4Me) \end{matrix}>CS$, yellow needles, m. p. 111°, and p-*tolyl*iso*amylparabanic acid*, $\begin{matrix} CO\text{——}N(C_5H_{11}) \\ CO\cdot N(C_6H_4Me) \end{matrix}>CO$, colourless needles, m. p. 90°.

In order to examine the action of cyanogen on a trisubstituted thiocarbamide, phenyldiethylthiocarbamide was taken; the only isolable product was thiocarbanilide, the formation of which was probably due to the decomposition of some unstable intermediate product.

When *m*-nitrobenzaldehyde and "thiocarbimidoacetic" acid were mixed into a paste with the gradual addition of sodium hydroxide, condensation occurred, with formation of "β-m-*nitrobenzylidenethiocarbimidoacetic acid*," $\begin{matrix} CO\text{——}S \\ NH\cdot CO \end{matrix}>C{:}CH\cdot C_6H_4\cdot NO_2$, pale yellow,

microscopic, rectangular plates, m. p. 277° (decomp.). Under similar conditions, thiohydantoin underwent condensation with *m*-nitrobenzaldehyde, giving β-m-*nitrobenzylidene*iso*thiohydantoic acid*, $NH_2\cdot C(:NH)\cdot S\cdot C(CO_2H):CH\cdot C_6H_4\cdot NO_2$, a colourless, crystalline solid, which, when recrystallised from acetic acid, was converted into 5-m-*nitrobenzylidene*iso*thiohydantoin*,

$$\begin{matrix} C(:NH)\cdot S \\ | \\ NH\text{---}CO \end{matrix}\!\!>C:CH\cdot C_6H_4\cdot NO_2,$$

yellow needles, m. p. 260°; the conversion of the former product into the latter also could be effected by heating to 200°. In a similar manner, thiohydantoin could be made to undergo condensation with piperonal, giving 5-mp-*methylenedioxybenzylidene*iso-*thiohydantoin*, $\begin{matrix} C(:NH)\cdot S \\ | \\ NH\text{---}CO \end{matrix}\!\!>C:CH\cdot C_6H_3<^{O}_{O}>CH_2$, yellow platelets, decomp. near 215°.

The method applied above for the condensation of aldehydes with thiohydantoin can be successfully substituted by heating the reagents with acetic acid and sodium acetate; thus, benzaldehyde and thiohydantoin under the latter conditions gave rise to β-benzylidene*iso*thiohydantoin, which has already been prepared by condensation in the presence of alkali (Kučera, A., 1914, i, 434).

When molecular quantities of di-*p*-hydroxyphenylthiocarbamide and chloroacetic acid were gently heated together, the substances reacted, with formation of 2:3-*di*-p-*hydroxyphenylthiohydantoin*, $CH_2<\begin{matrix} S\text{---}C:N\cdot C_6H_4\cdot OH \\ | \\ CO\cdot N\cdot C_6H_4\cdot OH \end{matrix}$, colourless, rhombic prisms, m. p. 236°.

Attempts to produce condensation products of thiodiglycollic acid with other aldehydes than benzaldehyde (Loven, A., 1885, 241) were fruitless except with salicylaldehyde, which in solution in boiling acetic acid in the presence of sodium acetate and acetic anhydride gave rise to 3:3′-*thiodicumarinyl*,

$$\begin{matrix} C_6H_4\cdot CH \\ | \\ O\text{——}CO \end{matrix}\!\!>C\cdot S\cdot C<\!\!\begin{matrix} CH\cdot C_6H_4 \\ | \\ CO\text{–}O \end{matrix},$$

very pale yellow needles, m. p. 288—289°.

*iso*Amylthiocarbimide can be readily prepared by the action of ethyl chlorocarbonate on potassium *iso*amyldithiocarbamate, which is obtained by mixing *iso*amylamine, carbon disulphide, and potassium hydroxide in molecular proportion in alcoholic solution.

In a footnote by R. Andreasch, it is reasserted that the compound obtained by desulphurisation of ethylthioparabanic acid (A., 1898, i, 243) was in reality ethylparabanic acid (compare Biltz and Topp, A., 1913, i, 600). D. F. T.

Partial Hydrolysis of Biscyanamides. J. VON BRAUN (*Ber.*, 1916, **49**, 2600—2605).—The author has succeeded in finding the conditions under which compounds of the type

$$CN\cdot NMe\cdot Ar\cdot CH_2\cdot Ar\cdot NMe\cdot CN$$

can be hydrolysed to substances of the formula

$$CN\cdot NMe\cdot Ar\cdot CH_2\cdot Ar\cdot NHMe,$$

which may prove to be of interest for further investigations. This partial hydrolysis is effected by concentrated hydrochloric acid at temperatures just below 100°, whereas the boiling acid causes complete hydrolysis.

pp'-Dicyanodimethyldiaminodiphenylmethane is hydrolysed to *pp'*-dimethyldiaminodiphenylmethane by boiling hydrochloric acid (A., 1904, i, 687) or to p-*methylamino*-p'-*cyanomethylaminodiphenylmethane*, m. p. 112°, as indicated. This forms a sparingly soluble hydrochloride and a pale yellow *nitroso*-compound, m. p. 121°. *pp'*-Dicyanodimethyldiaminodi-*o*-tolylmethane yields either pp'-*dimethyldiaminodi*-o-*tolylmethane*, leaflets, m. p. 81—82°, which forms a *platinichloride*, decomp. 220°, a *benzoyl* derivative, m. p. 118°, a *phenylthiocarbamide*, m. p. 171°, and a *dinitroso*-compound, yellow leaflets, m. p. 105—106°, or p-*methylamino*-p'-*cyanomethylaminodi*-o-*tolylmethane*, m. p. 89—90°, which gives a yellow *nitroso*-compound, m. p. 93—94°. 2:4'-Dicyanodimethyldiaminophenyl-*m*-tolylmethane forms 2:4'-*dimethyldiaminophenyl*-m-*tolylmethane*, m. p. 57°, which yields a *diacetyl* compound, m. p. 124°, and a *dinitroso*-compound, m. p. 101°. This may be reduced to a *dihydrazine*,

$$NH_2{\cdot}NMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_3Me{\cdot}NMe{\cdot}NH_2$$

m. p. 104—105°, which does not, apparently, condense with ketones, but gives crystalline hydrazones with many aldehydes (for example, derivatives of formaldehyde, m. p. 140°; heptaldehyde, m. p. 54°; benzaldehyde, m. p. 220°; arabinose, m. p. 165°; galactose, m. p. 180°; rhamnose, m. p. 159°). Partial hydrolysis of the same biscyanamide apparently affects the group in the para-position; 2-*cyanomethylaminophenyl*-4-*methylamino*-m-*tolylmethane* has m. p. 111—112°, and forms a *picrate*, m. p. 173°, a *benzoyl* derivative, m. p. 100°, and a *nitroso*-compound, glistening, yellow leaflets, m. p. 105°. J. C. W.

***tert.*-Aminobenzyl Alcohols and their Derivatives. V. Basic Derivatives of Benzophenone.** J. VON BRAUN (*Ber.*, 1916, **49**, 2605—2608).—Although *pp'*-tetramethyldiaminodiphenylmethane can be readily oxidised by chloranil to Michler's ketone (Kliegl, A., 1906, i, 433), such is not the case with other basic diphenylmethane derivatives in which one at least of the positions adjacent to the methylene bridge is occupied by a hindering group, such as the methyl or dimethylamino-groups. These compounds can, however, be converted into the benzophenones, the unsymmetrical ones having considerable interest, by the method developed in the cases of tetramethyldiaminodiphenylmethane (A., 1904, i, 687) and tetramethyldiaminoxanthen (A., 1916, i, 663).

Thus 2:4'-tetramethyldiaminophenyl-*m*-tolylmethane is converted into the dicyanodimethyldiamine, and this is oxidised by chromic acid to 2 : 4'-*dicyanodimethyldiaminophenyl* m-*tolyl ketone*, $CN{\cdot}NMe{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3Me{\cdot}NMe{\cdot}CN$, which crystallises in felted needles, m. p. 237°, and forms an *oxime*, m. p. 177°. The ketone is hydrolysed by boiling with concentrated hydrochloric acid to 2 : 4'-*dimethyldiaminophenyl* m-*tolyl ketone*, a bright,

yellowish-green powder, m. p. 133°, which forms a pale yellow *platinichloride*, decomp. 290°, a *benzoyl* derivative, m. p. 202°, and a pale yellow *dinitroso*-compound, m. p. 221°, and may be converted by means of methyl iodide into the desired 2 : 4′-*tetramethyldiaminophenyl* m-*tolyl ketone*, $NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_3Me \cdot NMe_2$, in leaflets, m. p. 143—144°.

Similarly, *pp*′-tetramethyldiaminodi-*o*-tolylmethane can be converted into pp′-*dicyanodimethyldiaminodi*-o-*tolyl ketone*,

$$(CN \cdot NMe \cdot C_6H_3Me)_2CO,$$

needles, m. p. 160°, and this into pp′-*dimethyldiaminodi*-o-*tolyl ketone*, m. p. 62—63°, which forms a pale yellow *dinitroso*-compound, m. p. 102°. J. C. W.

***tert*.-Aminobenzyl Alcohols and their Derivatives. VI. Trioxymethylene and Dimethyl-*o*-toluidine.** J. von Braun and K. Heider (*Ber.*, 1916, **49**, 2608—2610).—In 1892, Alexander heated some dimethyl-*o*-toluidine with trioxymethylene and dilute zinc chloride solution in sealed tubes at 170—180° for several hours, and obtained a non-volatile base which he supposed had the formula $(NMe_2 \cdot C_6H_4 \cdot CH_2)_2CH_2$. The authors have re-examined this subject, and find that the only non-volatile base (25% yield) is 4 : 4′-tetramethyldiaminodi-*m*-tolylmethane,

$$(NMe_2 \cdot C_6H_3Me)_2CH_2$$

(A., 1913, i, 1327). J. C. W.

Ethylene Dibromide and Dimethylaniline. J. von Braun and Z. Arkuszewski (*Ber.*, 1916, **49**, 2610—2612).—Schoop (A., 1881, 160) obtained a non-volatile base by warming together dimethylaniline and ethylene dibromide, and this is still regarded as *pp*′-tetramethyldiaminodiphenylethane. It is now shown, however, that the base is really Fröhlich's ethylenedi-methylaniline [diphenyldimethylethylenediamine] (A., 1907, i, 347). Apparently, a quaternary bromide is first formed, which then parts with methyl bromide, thus: $2C_6H_5 \cdot NMe_2 + C_2H_4Br_2 = (Br \cdot NMe_2Ph)_2C_2H_4 = (NMePh)_2C_2H_4 + 2MeBr$.

Characteristic of this diphenyldimethylethylenediamine, and the similar tri-, tetra-, and penta-methylene compounds, is the fact that they are readily oxidised by traces of many oxidising agents to very highly coloured (greenish-blue to reddish-blue) substances, which are receiving further attention. J. C. W.

Constitution of Isatide. Moritz Kohn (*Ber.*, 1916, **49**, 2514—2515. Compare Heller, A., 1916, i, 753).—Kohn does not recognise in Heller's arguments in favour of a quinhydrone formulation for isatide any reasons for abandoning his pinacone formula. J. C. W.

Some α-Styrylbenziminazoles and their Azo-dye Derivatives. O. Kym and S. Jurkowski (*Ber.*, 1916, **49**, 2681—2697).—In a number of papers since 1899, Kym has referred to the influence of various substituents on the colour of

2-phenylbenziminazoles and azo-dyes derived from them. It is now shown that corresponding styryl compounds are decidedly deeper in colour, and that amino- and nitro-derivatives of 2-styrylbenziminazole will even dye cotton fibres directly, to a certain extent. The styryl derivatives are readily obtained by the condensation of aldehydes with 5-nitro-2-methylbenziminazole, which is conveniently prepared by heating *p*-nitro-*o*-phenylenediamine with acetic anhydride and hydrolysing the acetyl compound so formed.

5-*Nitro-2-styrylbenziminazole*, $NO_2\cdot C_6H_3<\substack{NH \\ N}>C\cdot CH:CHPh$, is obtained by condensation with benzaldehyde, in golden-yellow needles, m. p. 90—95°, or by boiling p-*nitro*-o-*phenylenedicinnamoyldiamine*, $NO_2\cdot C_6H_3(NH\cdot CO\cdot CH:CHPh)_2$ (bulky, silver-white needles, m. p. 250—251°), with aqueous-alcoholic sodium hydroxide. This is reduced by tin and hydrochloric acid to 5-*amino-2-styrylbenziminazole*, which crystallises in bundles of pale yellow needles, m. p. 195—200°, and exhibits in alcoholic solution the intense pale green fluorescence characteristic of aminobenziminazoles. The 5-*acetylamino*-compound forms slender needles, m. p. 283°, and exhibits pale bluish-violet fluorescence.

5-*Nitro*-2-p-*nitrostyrylbenziminazole*, obtained by heating with the aldehyde at 180—210°, crystallises in deep yellow needles, m. p. above 300°, and forms a cinnabar-red *sodium* salt and a pale yellow *hydrochloride*. 5-*Amino*-2-p-*aminostyrylbenziminazole* forms heavy, sandy, yellow crystals, m. p. 237—238°, and dissolves in acids or sodium hydroxide.

Comparative tests were made on the tinctorial properties of the azo-dyes obtained by coupling the above amines with diazotised 2-naphthol-3 : 6-disulphonic acid (R) and 8-amino-1-naphthol-3 : 6-disulphonic acid (H) (see D.R.-P., 288190, of 1914). The dyeing of cotton directly by all of the above derivatives in alkaline baths is also described.

5-*Nitro*-2-p-*hydroxystyrylbenziminazole* crystallises in orange-red flocks, m. p. above 300°; 5-*nitro*-2-mp-*dihydroxystyrylbenziminazole* forms brownish-yellow flocks, m. p. 271°; 5-*nitro*-2-m-*hydroxy*-p-*methoxystyrylbenziminazole* also forms orange-coloured flocks, m. p. 278—279°. Isatin also gives a condensation *product*, $NO_2\cdot C_6H_3<\substack{NH \\ N}>C\cdot CH:\underset{|}{\overset{CO\cdot NH}{C}}{-}C_6H_4$, in small, cinnabar-red, glistening crystals, m. p. above 300°, but phenanthraquinone forms an abnormal, dark green *product*, m. p. 256—258°. J. C. W.

The Hydrolysis of Methyl-*tert.*-butyl- and Dimethyl-*tert.*-butyl-triaminobenzene. J. HERZIG and F. WENZEL (*Monatsh.*, 1917, **37**, 567—585).—Although 2 : 4 : 6-trinitro-1-methyl-3-*tert.*-butylbenzene can be easily reduced to the corresponding amino-compound, the further conversion of this product into the corresponding substituted phloroglucinol is rendered difficult

by the tendency of the tertiary butyl radicle to undergo scission from the compound.

[With E. TAIGNER.]—Commercial trinitromethylbutylbenzene, after purification by recrystallisation, was reduced with tin and hydrochloric acid to 2 : 4 : 6-triamino-1-methyl-3-*tert.*-butylbenzene *hydrochloride*, $C_4H_9{\cdot}C_6HMe(NH_2)_3,3HCl$, colourless needles, which rapidly undergoes atmospheric oxidation, and gives a deep red coloration with ferric chloride solution. When warmed with acetic anhydride, the amino-compound was acetylated, with scission of one amino-group, the product being *diacetyldiaminoacetoxy*-1-*methyl*-3-tert.-*butylbenzene*, $C_4H_9{\cdot}C_6HMe(NHAc)_2{\cdot}OAc$, colourless, granular crystals, m. p. 268—270°, which on hydrolysis with hydrochloric acid yielded *diaminohydroxy*-1-*methyl*-3-tert.-*butylbenzene*, $C_4H_9{\cdot}C_6HMe(NH_2)_2{\cdot}OH$ (*dihydrochloride*, colourless needles, decomp. near 315°); this hydrochloride, when heated in boiling water in an atmosphere of carbon dioxide for several hours, underwent hydrolysis, with formation of methylphloroglucinol, the *tert.*-butyl group having been eliminated. Methylphloroglucinol was found to yield a triacetyl derivative capable of existence in two forms, m. p. 52° and 76° respectively (compare Weidel, A., 1898, i, 578).

[With A. KICHLER.]—2 : 4 : 6-Trinitro-1 : 3-dimethyl-5-*tert.*-butylbenzene, when reduced with tin and hydrochloric acid, suffers partial loss of the butyl radicle, *diaminohydroxy*-m-*xylene dihydrochloride*, $OH{\cdot}C_6HMe_2(NH_2)_2,2HCl$, needles [*penta-acetyl* derivative, $OAc{\cdot}C_6HMe_2(NAc_2)_2$, colourless crystals, m. p. 122—123°], and *triamino*-m-*xylene trihydrochloride*, $C_6HMe_2(NH_2)_3,3HCl$, colourless crystals [*hexa-acetyl* derivative, $C_6HMe_2(NAc_2)_3$, needles, m. p. 192—194°], accompanying the normal product, namely 2 : 4 : 6-*triamino*-1 : 3-*dimethyl*-5-tert.-*butylbenzene trihydrochloride*, $C_4H_9{\cdot}C_6Me_2(NH_2)_3,3HCl$, colourless crystals; this substance, when hydrolysed by boiling with water in an atmosphere of carbon dioxide, behaved in an analogous manner to its lower homologue, giving dimethylphloroglucinol (Weidel and Wenzel, A., 1898, i, 579, 580), together with some *aminodihydroxy*-m-*xylene* [*tri-acetyl* derivative, $NHAc{\cdot}C_6HMe_2(OAc)_2$, rhombic crystals, m. p. 113—114°].

When eliminated in the above manner, it is probable that the *tert.*-butyl radicle forms trimethylcarbinol. D. F. T.

The Isomeric 3-Methyluric Acids. EINAR BIILMANN and JOHANNE BJERRUM (*Ber.*, 1916, **49**, 2515—2522).—A critical examination has been made of the crystalline form, absorption spectra, solubility, and acid strength of the α-, δ-, and ζ-forms of 3-methyluric acid. In agreement with Fischer and Ach (1899), it is found that the α-acid, which is best prepared by Grohmann's method (A., 1911, i, 691), certainly differs in outward appearance from the δ-acid (Loeben, 1897) and the ζ-acid (Fischer and Ach), which are crystallographically identical. The three acids give almost exactly the same absorption curves for ultra-violet light as uric acid itself, so they can scarcely differ in any profound struc-

tural way. The H-ion concentration of $27 \cdot 5 \times 10^{-5}$ molar solutions of the α-, δ-, and ζ-acids was found by a colorimetric method to be $0 \cdot 22 \times 10^{-5}$ for the first and slightly less than $0 \cdot 11 \times 10^{-5}$ for the others, whilst the resistances of the same solutions in a certain apparatus were 20,670, 29,967, and 29,654 ohms respectively, that of uric acid of the same concentration being 19,080 ohms. The solubilities of the acids in water at 25° are 0·0162, 0·0054, and 0·0055 gram per 100 grams of solution.

The only indication of a difference between the δ- and ζ-acids is the fact that the latter is more readily attacked than the former (or the α-acid) by phosphoryl chloride (Fischer and Ach). Even if this should prove to be due to some hitherto unrecognised catalytic influence, there would still remain the difficulty of explaining the existence of two different 3-methyluric acids. The α- and δ-acids are certainly not polymorphic, for they crystallise separately from mixtures and cannot be changed one into the other by inoculation. They undoubtedly have the methyl groups in position 3, for they all yield the same *thioluramil*,

$$CO<\begin{matrix}NH——CO\\NMe\cdot C(SH)\end{matrix}>C\cdot NH_2,$$

on heating with ammonium sulphide in a sealed tube (compare Fischer and Ach, A., 1896, i, 141). This compound forms elongated, straight-sided, colourless crystals, which are remarkably doubly refractive, the indices being 1·558 and 1·93. The α-acid, however, gives a poorer yield and reacts more sluggishly than the others. J. C. W.

Diazo-compounds. XIV. Decomposition of Derivatives of Ethyl Diazoacetate by Heat. H. Staudinger and H. Hirzel (*Ber.*, 1916, **49**, 2522—2529. Compare A., 1916, i, 847—856).—Benzoylphenyldiazomethane decomposes on heating into diphenylketen (*ibid.*, 854). The action of heat on the diazoacylacetates and similar esters, which are readily formed by treating ethyl diazoacetate with acyl chlorides (*ibid.*, 855), has therefore been examined, in the hope of obtaining esters of ketencarboxylic acids. In most cases, however, substituted malonic esters are formed, but their production can be traced back to an inexplicable action of heat on the expected ketens. By carrying out the decomposition at as low a temperature as possible, for which boiling with xylene and some platinum chips usually serves, the intermediate ketens can, however, frequently be isolated.

Thus, if ethyl diazobenzoylacetate is heated alone at 250°, it yields ethyl phenylmalonate, but if the corresponding methyl ester is boiled with xylene as indicated, nitrogen is evolved quantitatively and the polymeride of the keten is left. When this is distilled, *methyl phenylketencarboxylate*, $CO:CPh\cdot CO_2Me$, is obtained as a lemon-yellow oil, b. p. 80—85°/0·2 mm. Similarly, ethyl diazoketosuccinate yields *ethyl ketendicarboxylate*, $CO:C(CO_2Et)_2$, b. p. 115—116°/11 mm., mixed with much ethyl methanetricarboxylate, when heated carefully at 250°, but the almost pure keten when boiled with xylene.

Quantitative evolution of nitrogen was also realised in the decomposition of some other esters, including a thiodiazole derivative, but the products are not described as they are not the expected ketens. J. C. W.

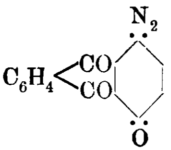
Action of Diazo-compounds on Copper Acetylide: Synthesis of Tetraphenylethane. V. V. SCHARVIN and N. I. PLACHUTA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 253—257).—According to Sandmeyer (A., 1884, 1311; 1885, 149), the interaction of copper acetylide and benzenediazonium chloride yields chlorobenzene, the action being a purely catalytic one brought about by the copper chloride resulting from the decomposition of the copper acetylide by the dilute acid; the acetylene, then, plays no part in the change. The authors' results show, however, that the acetylene does participate in the reaction, and that its carbon atoms enter into the hydrocarbon synthesised. In order to prevent the copper acetylide from floating on the surface of the liquid, the latter must be kept thoroughly mixed.

The action of benzenediazonium chloride (or *p*-nitrobenzenediazonium chloride) on copper acetylide yields a large proportion of chlorobenzene or *p*-chloronitrobenzene, and although other products are formed, chlorine is found in all the fractions distilled. With copper acetylide and benzenediazonium sulphate, the products obtained are: (1) a little phenol, (2) diphenyl, and (3) tetraphenylethane, the formation of which takes place according to the following equation: $4N{:}NPh{\cdot}SO_4H + 2Cu{\cdot}C{:}C{\cdot}Cu = CHPh_2{\cdot}CHPh_2 + C_2H_2 + 4N_2 + 4CuSO_4$. The secondary reaction yielding diphenyl is expressed thus: $2N{:}NPh{\cdot}SO_4H + Cu{\cdot}C{:}C{\cdot}Cu = C_6H_5Ph + C_2H_2 + 2N_2 + 2CuSO_4$.

In the case of silver acetylide and a diazonium salt, there is no reaction, neither marked evolution of gas, nor change in character of the precipitate, nor passage of the silver into solution occurring. T. H. P.

Anthraquinone-1-diazonium Haloids. ALFRED SCHAARSCHMIDT (*Ber.*, 1916, **49**, 2678—2681).—*Anthraquinone*-1-*diazonium chloride* is remarkably stable, and can be obtained readily by diazotisation of a suspension of the pale grey hydrochloride of 1-aminoanthraquinone at 30—40°, and crystallisation from brine at 85—90°. It separates in pale brownish-yellow, glistening platelets. The golden-yellow *bromide* is formed by "salting-out" with potassium bromide; it will keep for weeks in a desiccator.

4-*Chloroanthraquinone*-1-*diazonium chloride* and *bromide* are even more stable. The former cannot be "salted-out," as it is too soluble; it is obtained by adding amyl nitrite to a suspension of the base in a mixture of glacial acetic acid and sufficient hydrochloric acid, and then diluting with ether. When warmed with dilute sodium acetate solution at 40—50°, it loses chlorine, and changes, apparently, into the *compound* (annexed formula), which



forms brownish-red needles. 1 : 4-Diaminoanthraquinone can be converted by the same means into *anthraquinone*-1 : 4-*bis-diazonium chloride*,

$C_{14}H_6O_2N_4Cl_2$,

which forms bundles of pale brownish-red needles. Anthraquinone-2-diazonium salts can be obtained in the same way. They are more unstable, and can be more easily converted into hydroxy-compounds, but they do not readily respond to Sandmeyer reactions. J. C. W.

Optical Activity of Albuminates of the Alkali Metals. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 265—268. Compare A., 1915, i, 1015).—Ammonium albuminate was prepared by treating a dilute aqueous albumin solution with ammonia and removing excess of the latter by evaporation to dryness. In order to prepare albuminates of the alkali metals, the dilute albumin solution is titrated with standard alkali hydroxide solution in presence of methyl-orange; equivalent proportions of the albumin and alkali solutions are then heated together at a temperature not exceeding 50°, the temperature of coagulation for a concentration of 1·5—3% being 56°. After careful evaporation of the solutions to dryness, the albuminates are treated with absolute alcohol to remove any possible trace of alkali. The albuminates prepared from non-coagulated albumin have the following specific rotations: ammonium, −64·51°, or, prepared in a sealed tube at about 50°, −67·56°; lithium, −44·87°; sodium, −51·09°; and potassium, −55·55°. Those prepared from coagulated albumin give the values: ammonium, −56·7°; lithium, −48·78°; sodium, −52·17°; and potassium, −57·09°. In this case, then, the ammonium compound has the highest rotation, whilst with the caseinogenates, glutinates, and nucleates the rotations increase in the order: lithium, ammonium, sodium, potassium. T. H. P.

Fibrin regarded as an Anisotropic, Amorphous, Solid Substance. H. Diesselhorst and H. Freundlich (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, **3**, 46—59).—The authors consider that fibrin belongs to the group of anisotropic, amorphous, solid substances which includes such substances as vanadium pentoxide. Hekma (A., 1914, i, 1013) has already shown that it forms sols and gels in which, on coagulation, particles are produced that, under the ultramicroscope, are seen to have a needle- or thread-like appearance. Many of the phenomena described by Hekma, such as the sudden appearance of fibrin needles after an incubation period and the growth of large needles by the fusion of amicronic particles, can be explained if the formation of fibrin is regarded as a coagulation with a subsequent growth of the coagulated particles, both reactions being of an autocatalytic nature and dependent on the kind and concentration of the coagulating agent. It is owing to the anisotropic, amorphous character of the fibrin particles that coagulation is aided by mechanical means, such as

stirring, which causes the fibrin needles to assume parallel positions, and thus enables them rapidly to join together to form fibres and threads. H. W. B.

Optical Activity of Gelatinates of the Alkali Metals: Chemistry of α- and β-Gelatins. M. A. Rakuzin and (Mlle.) Ek. Maks. Braudo (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 269—272).—Ammonium α-(or β-)gelatinate was prepared by the action of ammonia on a dilute (less than 0·75%) solution of gelatin (or β-gelatin), either in the cold or at the boiling point under the ordinary or increased pressure. The gelatin or β-gelatin solution was titrated with decinormal sodium hydroxide in presence of phenolphthalein, and the lithium, sodium, and potassium gelatinates prepared by boiling the gelatin or β-gelatin solution with the equivalent proportion of the corresponding hydroxide solution. The dry gelatinates were treated with absolute alcohol to remove any possible trace of free alkali. The specific rotations are as follows: α-Gelatin, −133·86°; lithium α-gelatinate, −83·33°; ammonium, −89·55°, or, when prepared under pressure, −100·00°; sodium, −101·85°; and potassium, −121·21°. β-Gelatin, −127·58°; lithium β-gelatinate, −84·74°; ammonium (prepared under pressure), −103·15°; sodium, −106·55°; potassium, −124·48°. T. H. P.

Adsorption of Toxins and Antitoxins by Aluminium Hydroxide: Koch's Tuberculin. I. M. A. Rakuzin and G. D. Flier (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 711—716).—Of the eight ordinary colour reactions of the proteins, the only one not given by tuberculin is the violet coloration with fuming hydrochloric acid (Liebermann's reaction); since, further, tuberculin contains phosphorus, it must be regarded as an analogue of casein. In aqueous solution, its specific rotation is $[\alpha]_D$ −14·62°. By adsorption with aluminium hydroxide, it is separated into (1) 4·44% of an adsorbed antitoxin, which gives only Molisch's and Ostromisslenski's reactions, and in composition and properties resembles pepsin, the latter giving only Molisch's reaction; (2) 95·56% of a non-adsorbed toxin which, like casein, gives the biuret, Millon's, xanthoprotein, Adamkiewicz's, Molisch's, Pettenkofer's, and Ostromisslenski's reactions. The adsorption is irreversible. T. H. P.

Optical Properties of Diastase and its Adsorption by Kaolin and by Aluminium Hydroxide. M. A. Razukin and G. D. Flier (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 321—324).—At 60°, only 84·12% of Merck's diastase is soluble in water; the solution is optically inactive, and gives the biuret, the xanthoprotein, Molisch's, and Ostromisslenski's reactions (compare A., 1915, ii, 602), the limits of sensitiveness being 1 in 1690, 840, 6660, and 750 respectively. In two diastase solutions, 7·19% and 7·10% of the total diastase present was adsorbed by aluminium hydroxide, and a second treatment with the latter effected no

further diminution in the specific gravity of the solution. Further, if the aluminium hydroxide is subsequently washed carefully and pressed, and then treated with hot water, the liquid shows none of the colour reactions of the original diastase solution; the adsorption is therefore irreversible. The adsorbed portion of the diastase fails to give Ostromisslenski's colour reaction with picramic acid. Since diastase consists of two enzymes, of which one converts starch into dextrins, whilst the other saccharifies it to maltose, it may be that the adsorbed and non-adsorbed parts correspond with these two constituents. Diastase is not adsorbed by the electronegative kaolin (compare Wo. Ostwald, "Grundriss der Kolloidchemie," 1909, 424). T. H. P.

Intermediate Compounds in the Hydrolysis of Fats by the Lipase of Ricinus Seeds. N. V. Tancov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 257—264. Compare A., 1914, i, 759).—From the results of further experiments, the conclusion is drawn that the intermediate compounds formed by the lipase with the acid products of the hydrolysis of fats are least stable at the optimum concentration of the activator (sulphuric acid), the velocity of the reaction evidently depending on the velocity with which these compounds decompose in the solution. Both the substrate and the acid products of its hydrolysis accelerate the formation of the activator in mixtures of the seeds with water, in just the same way as the activator accelerates the scission of the substrate. T. H. P.

Mode of Action of Urease and of Enzymes in General. K. George Falk (*J. Biol. Chem.*, 1917, **28**, 389—390. Compare Van Slyke and Cullen, A., 1914, i, 1181, and succeeding abstract).—The author disputes the general validity of Van Slyke and Cullen's equation expressing the rate of enzyme action. H. W. B.

Mode of Action of Urease and of Enzymes in General. Donald D. Van Slyke and Glenn E. Cullen (*J. Biol. Chem.*, 1917, **28**, 391. Compare preceding abstract).—Polemical. H. W. B.

Physiological Chemistry.

Elements which Condition the Activity of Glycolytic Enzymes. I. The Glycolytic Enzymes of the Pancreas, and Blood Corpuscles. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 461—466).—When dextrose (about 1%) is dissolved in Tyrode's liquid and the solution circulated in the

pancreas and then placed in a thermostat, no diminution occurs in the proportion of dextrose present. Addition of blood corpuscles to the solution causes, however, a marked diminution in the reducing power, this being due, not merely to simple molecular condensation of the dextrose, but to its destruction. If the circulation in the pancreas is omitted, the content of dextrose in the liquid remains unchanged after blood corpuscles have been added. It is evident that, under the above experimental conditions, the pancreas emits a glycolytic enzyme into the circulating liquid, but that this enzyme manifests its maximal activity only with the aid of other factors, such as blood corpuscles. T. H. P.

Processes of Adsorption in Chemotherapeutics and Immunity. N. ANDREEV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 222—251).—As the majority of the constituent parts of the animal organism consist of colloids, the mechanism of many of the processes proceeding in it may be well explained from the point of view of the phenomena characteristic of disperse systems. Such explanations exist for metabolic changes, for the physiology of nutrition, for certain pathological phenomena, for the reaction between immune substances, etc., and the author extends them as forming the basis of chemotherapeutics and immunity.

In their relations to electrolytes and to cataphoresis, bacteria may be regarded as coarsely disperse of the suspensoid, emulsoid, or intermediate type with, in most cases, negative charges. Under the influence of an electric current, protozoa, like most amœbæ, exhibit positive charges. Since Ehrlich's arsenical preparations, containing arsenic as anion, have a therapeutic action on protozoa, but no curative effect on bacterial diseases, which are, however, influenced by preparations with poisonous cations, the conclusion is drawn that a process of electrical adsorption forms the foundation of chemotherapeutics. The ability of bacteria to change their charge under certain conditions allows of the application of Ehrlich's compounds to the cure of bacterial diseases.

That anti-substances may be regarded as globulins follows from the analogous relations of proteins and anti-toxins to physical and chemical factors, the ability of substances of both these types to adsorb irreversibly antigens, the high adsorptive power of serum proteins towards globulins, the precipitability of anti-substances from immune sera by globulins, and the absence of increase in the proteolytic enzymes in blood after injection of immune serum of an animal of the same kind.

The ability of proteins to decompose, yielding basic products which give rise to a specific anti-substance on immunisation, the formation of neutral compounds of toxins with acids, the rate of diffusion through gelatin, and the partial passage through animal membranes, justify the conclusion that toxins are products of the scission of proteins which are semi-colloidal in their physico-chemical relations. Evidence is adduced which indicates that mechanical adsorption, with its characteristic selectivity, forms the basis of specificity. T. H. P.

Influence of the Coagulation by Rennin on the Gastric Digestion of the Proteins of Milk. J. T. LEARY and S. H. SHEIB (*J. Biol. Chem.*, 1917, **28**, 393—398).—The proteins of milk are most easily digested by the gastric juice when the caseinogen has been previously precipitated by the addition of dilute hydrochloric acid to the whole milk. The addition of oxalate to the milk to prevent clotting is inadvisable, because the oxalate also slightly inhibits the action of the pepsin. The thick, elastic curd produced when milk curdles is only slowly attacked by gastric juice. Boiled milk is digested rather more quickly than unboiled milk. H. W. B.

Comparative Biochemistry of Purine Metabolism. III. The Presence of Allantoin in Mammalian Blood. ANDREW HUNTER (*J. Biol. Chem.*, 1917, **28**, 369—374).—Allantoin has been isolated by the author from the blood of the ox and the pig, and identified by its crystalline form and melting point. Traces of allantoin were also detected in the blood of the horse and the sheep, but not in human blood. H. W. B.

Infant Feeding. The Chemical Changes produced by the Addition of Calcium Hydroxide to Milk. A. W. BOSWORTH and H. I. BOWDITCH (*J. Biol. Chem.*, 1917, **28**, 431—435).—The addition of calcium hydroxide to milk, which normally contains some insoluble calcium hydrogen phosphate (Van Slyke and Bosworth, A., 1915, i, 192), results in the precipitation of more calcium phosphate, the insoluble phosphates under these conditions being a mixture of the di- and tri-calcium phosphates. The reaction of the milk-serum is also brought towards the neutral point, the alkalinity of the calcium hydroxide being neutralised by the formation of the insoluble phosphates.

When applied to infant feeding, the milk is usually treated with lime water, and then diluted with an equal bulk of water. In these circumstances, owing to the precipitation of calcium phosphate, the soluble calcium and phosphorus in the diluted milk may be reduced to amounts less than those which are present in human milk. H. W. B.

Effects of Feeding the Proteins of the Wheat Kernel at Different Planes of Intake. E. V. MCCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1916, **28**, 211—229. Compare Hart, Miller, and McCollum, A., 1916, i, 581).—Feeding experiments on rats confirm the conclusions previously drawn from the results obtained from wheat-fed pigs. A diet containing a relatively large proportion of wheat is injurious, not to the animals themselves, but to their offspring. Normal growth may be secured on a diet containing from 6% up to 40% of wheat protein, but either reproduction does not occur, or the young invariably die within a few days of birth. The results are illustrated by numerous charts. H. W. B.

Is Lysine the Limiting Amino-acid in the Proteins of Wheat, Maize, or Oats? E. V. McCollum, N. Simmonds, and W. Pitz (*J. Biol. Chem.*, 1917, **28**, 483—499).—Rats are fed on wheat, maize, or oats as the sole source of protein, together with inorganic salts and butter fat, so that the diet is capable of promoting growth and general well-being, but the protein is too low in amount to enable growth to occur at the normal rate. The diets are then supplemented with either zein, which lacks tryptophan and lysine, or gelatin, which contains 6% of lysine, but neither tyrosine nor tryptophan. It is found that neither zein nor gelatin can sufficiently supplement the proteins of maize, so that the failure of maize adequately to promote growth is not due to a lack of lysine. On the other hand, gelatin added to either wheat or oats greatly improves its growth-promoting properties, whereas zein exerts a beneficial influence when combined with oats, but does not render wheat more efficient for the promotion of growth. It is possible, therefore, that lack of sufficient lysine accounts for the inadequacy of wheat protein, but in the case of oats, neither lysine, tyrosine, nor tryptophan can be the limiting amino-acid, of which the minimal amount present determines the abnormally low rate of growth. H. W. B.

Mechanism of Cytolysis in Sea-urchin Eggs. A. R. Moore (*J. Biol. Chem.*, 1917, **28**, 475—482).—The cytolysis of the fresh, unfertilised eggs of the sea-urchin by hot water can be represented as a process proceeding at the rate of a unimolecular reaction. Since strontium ions are found to act as a positive catalyst of this reaction, it is probable that the action of strontium ions in sensitising sea-urchin eggs to foreign sera and to starfish sperm is also due to catalysis of the cytolysis reaction.

H. W. B.

Proteins of the Central Nervous System. H. M. McGregor (*J. Biol. Chem.*, 1917, **28**, 403—427).—The nervous tissue (sheep's brain) is dried in thin layers in a vacuum at 0°, and is then extracted with a mixture of benzene and alcohol, which extracts about 45% of the dry tissue. About 10% of the dry, fat-free residue consists of a *protein* containing iron and 0·11% of phosphorus. It is soluble in water, and is characterised by its instability. In the presence of weak acids, it is decomposed into at least three products, the natures of which are dependent on the nature and concentration of the acid employed. The protein obtained by different methods invariably contains iron.

A second *protein* is extracted from the dry, fat-free nervous tissue by dilute alkali hydroxide solutions. It also contains iron and 0·6% of phosphorus, and is present to the extent of approximately 10% of the dry tissue. It differs in properties from the protein extracted by water, and is precipitated completely by the addition of acid without decomposition.

The supporting tissue is insoluble in neutral, acid, or alkaline solvents, and consists, presumably, of a neurokeratin or scleroprotein. It comprises 20% of the dry tissue.

The brains of the ox, rabbit, sheep, dog, and man contain similar proteins. The same distribution of similar proteins occurs in each portion of the brain, namely, in the cerebrum, cerebellum, medulla, and pons of sheep's brain. H. W. B.

Metabolism of Dextrose in Surviving Organs. II. Action of the Pancreas on Dextrose Circulating in it. CAMILLO ARTOM (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 466—471. Compare Lombroso, this vol., i, 102).—When blood containing dextrose is circulated in the pancreas of the dog, its reducing power always undergoes a diminution, which varies in amount in different cases, and may reach about 50%. The proportion of carbohydrates in the pancreas itself usually increases, but the amount of the increase is never greater than corresponds with about 55% of the quantity of dextrose disappearing from the blood. Tyrode's solution containing dextrose also loses in reducing power when circulated through the pancreas, but the loss is always less than with blood, and never exceeds 24%; a large part, sometimes more than 85%, of this loss is accounted for by increase in the proportion of carbohydrates in the pancreas. The behaviour of the pancreas in these two cases is in accord with that of the intestine. That more variable results are obtained with the pancreas is explained by the difficulty of maintaining the cellular elements in a state of functional integrity under artificial experimental conditions. The glycolytic activity of the pancreatic tissue becomes greater as the conditions employed approach more nearly to those in which the tissue exists in the living organism. T. H. P.

Metabolism of Dextrose in Surviving Organs. III. Action of the Spleen on Dextrose Circulating in it. CAMILLO ARTOM (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 513—516). —When blood containing dextrose is circulated in dog's spleen, the reducing power of the blood is diminished to an extent which varies in different cases, and may amount to 25%. At the same time, the carbohydrate content of the spleen increases, but such increase never accounts for more than 70% of the dextrose which disappears from the blood. With Tyrode's solution containing dextrose, a similar diminution in the reducing power occurs during circulation in the spleen, such diminution being greater than the simultaneous increase in the amount of carbohydrates in the spleen itself. T. H. P.

The Normal Content of Arsenic in Urine. PETER KLASON (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 6, 1—6).—In a previous paper (A., 1915, ii, 649), the author has described a method for the oxidation, by means of nitric acid, of organic liquids containing arsenic. An improved form of apparatus is now described, and full details are given of the manipulation necessary for the estimation of the arsenic content of urine.

The author has never taken arsenic in any form, nor has he suffered from "arsenic sickness"; nevertheless, from investigations made on himself, he finds that the urine always contains arsenic to the extent of 0·005—0·0125 mg. per litre. He draws the conclusion that arsenic is a normal constituent of the human body, and consequently its use as a medicine (compare iron) can be understood. It is probably introduced in the food taken, and in much greater quantity than could come from wallpapers, carpets, clothing, etc.

It is stated that the methods which have hitherto been used for the estimation of arsenic in organic secretions are so inexact that the results obtained are worthless. T. S. P.

Localisation of the Processes of Oxidation in the Cell and the Modifications Induced by Combinations of Electrolytes. VICTOR SCHLÄPFER (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, **3**, 1—45).—In general, a definite relationship exists between the weight of a rabbit and the amount of a dye which it is capable of receiving without the production of toxic effects. To account for this fact, the theory is advanced that the reducing power of living tissue is limited, being in the full-grown animal equivalent to 0·025 gram of dye per kilo. of tissue, whilst it is the unreduced dye which exerts the toxic action. Hence the amount of a dye which can be injected into an animal without the production of toxic effects is a measure of the oxidation occurring at the expense of the dye in the living tissue of the animal. It is further found that less reduction occurs when the animal is in a feverish condition; extirpation of the kidneys, testes, thyroid, and parathyroid glands in each case produces a similar effect. The inhibition of the processes of oxidation observed after these operations can also be produced by the simple injection of a solution of an ammonium salt. On the contrary, the introduction of salts of sodium or lithium accelerates the processes of oxidation in the cell, and, after any of the above operations, prevents the appearance of toxic symptoms after the injection of small quantities of a dye. In other words, those ions, sodium and lithium, which increase the excitability of muscle and nerve also stimulate the oxidation processes in the cell, whilst in each case the ammonium ion produces the reverse effect. H. W. B.

Influence of Inositol on the Excretion of Phenol in the Dog. HARRY DUBIN (*J. Biol. Chem.*, 1917, **28**, 429—430).—The ingestion of inositol does not lead to an increase in the amount of phenol excreted by the dog. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Loss in Alcoholic Fermentation. L. LINDET (*Compt. rend.*, 1917, **164**, 58—61).—If, in the fermentation of sugar, the yeast is supplied with an entirely mineral food containing ammonium sulphate, the loss of sugar is equal to about seventeen times the weight of yeast collected, two-thirds of the loss being in the form of carbon dioxide. If, however, to the solution other carbohydrates, such as gum arabic, rye-gum, or the humic substances of peat, are added to the extent of 2%, the fermentation becomes more rapid, the weight of yeast gathered is increased three times, and the ratio of loss of sugar to yeast gathered is only about one-third of that in the previous case. If a medium such as peptonised meat or gluten or yeast bouillon is used as a food supply for the yeast, the amount of yeast collected is about the same as in the previous case, but the loss of sugar per unit weight of yeast is much smaller. The sucrose is a poor nutrient for the yeast, ammonium salts in its presence only being with difficulty converted into protein. W. G.

Fermentation of Dibasic Acids. I. Malic Acid. A. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 725—748).—In presence of yeast, malic acid is, to some extent, decomposed, with formation of lactic acid.

The separation and estimation of lactic acid in presence of malic acid by Kunz's method (A., 1901, ii, 700) gives quantitative results if 3 vols. of 96% alcohol instead of 2 vols. of 95% alcohol are added per 1 vol. of solution; further, this addition must be made in small portions and with constant shaking, since otherwise the barium lactate is partly precipitated.

Attention is directed to the presence in commercial ether of acetaldehyde, alcohol, acetic acid, etc., this being regarded as the source of the acetaldehyde detected by Buchner and Langheld (A., 1913, i, 944) in sugar solution fermented by means of yeast juice in presence of a phosphate.

Experiment shows that, in 2% concentration, malic acid is readily fermented by yeast, the decomposition it undergoes being, however, more profound than that represented by the equation $CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H = CO_2 + OH{\cdot}CHMe{\cdot}CO_2H$. When its concentration is 4%, malic acid is only feebly fermented, evidently owing to the high acidity of the solution.

All the results obtained show that the initial stage in the fermentation of malic acid consists in the scission of carboxyl from the group, $CO_2H{\cdot}CH_2{\cdot}$, this change being perfectly analogous to the breaking of the aldol linking. On this account, the author regards the carboxylase concerned, which is possibly not identical with the carboxylase of Neubauer and Neuberg, as belonging to the group of the aldolases. Such enzymes have not yet been

isolated, but undoubtedly exist, as is shown by the lactic and alcoholic fermentations of the hexoses, in which a chain of six carbon atoms is broken into two chains of three carbon atoms. It might be expected that many, if not all, dibasic acids containing the group $CO_2H\cdot CH_2$ would be decomposed by carboxylase, and the same might be expected of polybasic acids, since citric acid is also readily fermented by yeast. In the fermentation of succinic acid, the latter appears to decompose, first, into carbon dioxide and propionic acid, but with malonic acid no decomposition is effected by yeast. The action of carboxylase is therefore specific.

In presence of methylene-blue, the fermentation of malic acid gives rise to acetaldehyde. It is found also that, in presence of acetaldehyde, a comparatively small proportion of the lactic acid undergoes oxidation to pyrotartaric acid. The results show that, if lactic acid is fermented to alcohol and carbon dioxide, such reaction is extremely slow, and must be regarded as a secondary one. From the fact that malic acid is dehydrated more slowly and feebly than lactic acid, it is supposed that in the decomposition of malic acid, carbon dioxide is first split off, the lactic acid being dehydrated as it is formed. T. H. P.

Investigation of the Influence of Climatic Conditions on the Composition of Plant Oils. G. V. Pigulevski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 324—341. Compare A., 1915, i, 758).—Evidence is adduced showing that, among plants belonging to one and the same sub-family, the iodine number of the essential oil increases as the geographical distribution of the plant extends further towards the north.

Plants of the families *Rosaceae*, *Ericaceae*, and *Pinaceae* yield oils containing the same acids. In the case of oleic acid, for which a number of isomerides are possible with different positions of the double linking, the natural acid is practically always the Δ^{θ}-acid, and the existence of this acid is doubtless related to its activity, since the activity varies considerably with the position of the double linking in the carbon chain.

The iodine number of an oil, characterising the degree of unsaturation, depends on the percentages of the triglycerides of unsaturated acids, and may be expressed by the formula

$$A_m = a_1x/100 + a_2y/100 + a_3z/100,$$

where A_m is the iodine number, x, y, and z are the percentages of the triglycerides of oleic, linoleic, and linolenic acids respectively, and a_1, a_2, and a_3, the corresponding iodine numbers of the triglycerides, have the respective values 86·2, 173·58, and 262·15. By means of this formula, a table has been constructed which shows how, for one and the same iodine number, the proportions of the three triglycerides may vary. T. H. P.

Humus Formation as an Essential Property of Plants. A. Troussov (*Bied. Zentr.*, 1916, **45**, 434—435; from *Selskoie Khoziaistvo i Lesovodstvo, Petrograd*, 1914, **74**, 233—246).—In a series of laboratory experiments, humus was obtained from various

organic compounds of vegetable origin by the action of acids and alkalis. The stages of the reaction are described as follows: Mono- and di-saccharides are first transformed into polysaccharides. Then, by a further loss of the elements of water, the molecules are broken down, and, after undergoing oxidation, finally yield humus. Where there is no oxidation, however, ulmin and ulmic acid are formed.

Humus is yielded by a mixture of aldehydes and polyhydric alcohols, but not by aldehydes alone, neither can it be obtained from pure ketones. The author considers that under natural conditions the stages are as described, but that micro-organisms take the place of acids and alkalis. Thus, the processes leading to humus formation consist of a perfectly definite series of chemical changes, and are not the result of an irregular destruction of molecules. L. M. U.

Effects of Large Applications of Commercial Fertilisers on Carnations. George D. Beal and Fred Weaver Muncie (*J. Amer. Chem. Soc.*, 1916, **38**, 2784—2804).—The fertilisers used were dried blood, sodium nitrate, ammonium sulphate, calcium superphosphate, disodium hydrogen phosphate, and potassium sulphate, sodium chloride and sulphate being used for comparison. The carnation cuttings were grown on selected soil, uniform throughout the benches, the watering, heating, ventilation, and illumination being as nearly identical as possible in each section. Weekly applications of the fertilisers at various rates were given on isolated sections from October 1st to May 1st, or until injury became serious. The easily soluble fertilisers produced almost immediate injury, the moderately soluble delayed injury, the sparingly soluble producing no apparent injury. The botanical injuries characteristic of an excess of each fertiliser are recorded.

An increase in the dry weight and ash content of the foliage is obtained with an increased application of each fertiliser, there being an increased content of the fertilising salt in the plant after large application to the soil. There is an increased intake of nitrogen when ammonium sulphate is applied, but the plant acquires a tolerance when successive small doses are applied. Injury from ammonium sulphate is not proportional to the total nitrogen content. Osmotic pressure determinations made on the sap, expressed from the stems after freezing, proved that with each fertiliser used the degree of injury varied with the osmotic pressure, this injury for a given osmotic pressure varying with the fertiliser used. Increase in osmotic pressure is not the exclusive cause of the plant injury. This increase is accompanied by an increase in the total solids and ash of the sap and in the amount of fertiliser taken up by the plant. There is an increase in the total acidity of the sap of plants fed on ammonium sulphate, disodium hydrogen phosphate, and monocalcium phosphate, phenolphthalein being the indicator, but none with potassium sulphate. Plants grown on soil to which large applications of potassium sulphate had been made gave a sap showing a higher total sugar content, as did also

extracts of the foliage. The starch content of the foliage of such plants was lower. W. G.

Proteins from the Jack Bean, Canavalia ensiformis. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1916, **28**, 67—75. Compare A., 1916, i, 357).—The jack bean contains two globulins which can be separated by fractional precipitation with ammonium sulphate. One of them, *canavalin*, has the composition C 53·26, H 7·03, O 22·51, N 16·72, and S 0·48%, and the other, *concanavalin*, C 53·28, H 7·02, O 22·15, N 16·45, and S 1·10%. After the removal of the globulins, the extract of the jack bean still contains protein, which has been isolated and found to be an *albumin* of the legumelin type with the composition C 53·24, H 7·00, O 22·50, N 16·38, and S 0·88%. H. W. B.

Some Constituents of Jambul. MERRILL C. HART and FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1916, **38**, 2805—2813). —An examination of the seeds of the Jambul tree (*Syzygium Jambolana*). The study of the resin gave, in general, the same results as those obtained by Power and Callan (compare A., 1912, ii, 480; 1913, i, 1057). The authors were able to obtain more conclusive evidence as to the presence, in the light petroleum extract, of myricyl alcohol, a hydrocarbon, probably hentriacontane, and of a phytosterol, $C_{27}H_{46}O$, m. p. 135—135·5°, giving an acetate, m. p. 119—120°. The ether and the chloroform extracts yielded a phytosterolin, m. p. 275—285°, giving an acetate, m. p. 167—168°. This was shown to be phytosterol *d*-glucoside. W. G.

Proteins of the Peanut, Arachis hypogæa. I. The Globulins Arachin and Conarachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1916, **28**, 77—87).—The peanut contains two globulins, *arachin*, C 52·15, H 6·93, O 22·23, N 18·29, S 0·40%, and *conarachin*, C 51·17, H 6·87, O 22·58, N 18·29, and S 1·09%. Conarachin contains 6·55% of basic nitrogen, which is the highest percentage of basic nitrogen recorded for any seed protein. Peanut press-cake may therefore prove to be highly effective in supplementing cattle-food products made from cereals and other seeds the proteins of which are deficient in basic amino-acids. H. W. B.

Saponin from Yucca filamentosa. L. H. CHERNOFF, ARNO VIEHOEVER, and CARL O. JOHNS (*J. Biol. Chem.*, 1917, **28**, 437—443).—The *saponin*, $C_{24}H_{40}O_{14}$, occurs as brown, amorphous masses in the fibrovascular bundles of the roots and leaf bases of *Yucca filamentosa*. It is obtained in the form of a white, amorphous powder by extraction of the dried roots with alcohol. On hydrolysis, it yields a *sapogenin*, crystallising in needles, m. p. 175°, together with dextrose and possibly glycuronic acid. Hæmolytic action was observed with the saponin, but not with the sapogenin. H. W. B.

The Characteristic Effect of Ammonium Salts on Plant Physiology. H. G. SÖDERBAUM (*Bied. Zentr.*, 1916, **45**, 454—455; from *Medd. No.* 125 *Centralanst. jordbruksförsök, Stockholm*, 1915, 13).—Phosphatic manures in the form of superphosphate, basic slag, and bone meal were applied to barley, with cross-dressings of sodium nitrate, ammonium sulphate, and ammonium chloride. Further, each plot was subdivided into three parts, two of which received magnesium salts (one the carbonate and the other the sulphate), whilst the third received no magnesium. The ammonium salts caused considerable depression of growth, especially when used with superphosphate, and to a less extent when used with bone meal. The leaves yellowed, and some plants died. With basic slag, however, the results were different; all plots were normal, as were all those which received magnesium carbonate; moreover, affected plots recovered rapidly with applications of magnesium carbonate, but not with magnesium sulphate. The author attributes the physiological disturbances of the plants not so much to any physiological acid reaction of the ammonium salts as to an actual toxic effect produced by them. L. M. U

Iodine Content of Food Materials. RALPH M BOHN (*J. Biol. Chem.*, 1917, **28**, 375—381).—Most food materials used in cattle feeding, such as hay, straw, oil meal, rock salt, and well water, contain only a minute trace, if any, of iodine. Kendall's method (A., 1914, ii, 815) was employed. H. W. B.

Efficiency of Certain Milk Substitutes in Calf Feeding. R. H. CARR, GEORGE SPITZER, R. E. CALDWELL, and O. H. ANDERSON (*J. Biol. Chem.*, 1917, **28**, 501—509).—The results indicate that various mixtures of animal and vegetable feeding materials are not as efficient as skim-milk for producing growth and development of the calf. H. W. B.

Dietary Deficiencies of the Maize Kernel. E. V. MCCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1916, **28**, 153—165. Compare Hart and McCollum, A., 1915, i, 39).—The experiments with pigs have now been repeated with rats, using the proteins of maize as the sole source of protein in the food. The results indicate that the proteins of maize contain all the amino-acids essential for growth, and also both the accessory factors termed "fat-soluble *A*" and "water-soluble *B*." The fat-soluble *A* is, however, present in relatively too small a proportion for maximum rate of growth to occur in rats without the addition of substances relatively rich in this factor, such as butter or other fats. The inorganic content of maize is also not suitable for the promotion of growth, and it is therefore necessary to add various salts to the rations before growth can take place. Even when the diet is supplemented in the manner indicated, the physiological well-being of the animal is not maintained throughout life, and it is considered doubtful whether a completely satisfactory diet can be derived entirely from the maize kernel as the sole source of protein.

H. W. B.

Organic Chemistry

The Thermal Decomposition of Low Temperature Coal Tar. DAVID TREVOR JONES (*J. Soc. Chem. Ind.*, 1917, **36**, 3—7. Compare Jones and Wheeler, T., 1915, **107**, 1318).—In an earlier paper (Jones and Wheeler, *loc. cit.*), an examination has been made of the nature of the tar obtained on distilling coal in a vacuum below 450°. The author has now investigated the thermal decomposition of this tar at temperatures between 550° and 800°, experiments being made by allowing the tar to flow over coke in a vertical tube of hard glass in an electric furnace, and also by distilling small quantities of the tar from a porcelain boat over porous porcelain in an atmosphere of carbon dioxide in a tube of hard glass or quartz.

As a result of the comparison of the composition of the distillate with that of the original tar and of the composition of the volatile product obtained at different temperatures, the following conclusions are drawn.

Ordinary coal-tar from coal at high temperatures is formed chiefly as the result of the decomposition of a tar previously formed at low temperature. The mechanism of the process consists essentially in the decomposition of the naphthenes, paraffins, and unsaturated hydrocarbons present in the low-temperature tar to form various olefines, which, at higher temperatures, condense to aromatic substances. The gaseous olefines of higher molecular weight are formed in maximum quantity at lower temperatures, their amount becoming negligible at 750°; this disappearance synchronises with the appearance of naphthalene, and immediately precedes a marked increase in the percentage of hydrogen. At medium temperatures, the formation of hydrogen is due to the decomposition of naphthenes, whilst the increase at higher temperatures is probably caused by the intermolecular and intramolecular condensation of aromatic compounds.

Phenols are primary products of coal distillation, but benzene and its homologues are produced in the secondary decomposition, chiefly as the result of olefinic condensation, but also, in part, by the thermal dehydrogenation of the corresponding naphthenes.

The part played by acetylene in coal-tar formation is insignificant (compare Meyer, A., 1912, i, 525). D. F. T.

Spinacene. A New Hydrocarbon from certain Fish Liver Oils. A. CHASTON CHAPMAN (T., 1917, **111**, 56—69).—In the examination of a reputed cod-liver oil, a remarkably high proportion of unsaturated hydrocarbon oil was found to be present, amounting to 89% of the total weight. This result is not due to any adulteration of the oil, but to the extraction of oil from the livers of two species of fish, *Centrophorus granulosus* and *Scymnus lichia*; these are caught off the Moroccan coast, and have only

recently come into the Portuguese market (compare Mastbaum, *Chem. Zeit.*, 1915, **39**, 139, 889; Tsujimoto, A., 1916, i, 786).

From the unsaponifiable portion of the oil, an optically inactive liquid hydrocarbon, *spinacene*, $C_{30}H_{50}$, b. p. 268—269°/10 mm., D_{20}^{20} 0·8616, n_D^{20} 1·4967, was separated by distillation; this substance yielded a *hexahydrochloride*, a *trihydrochloride*, a *dodecabromide*, a *trinitrosochloride*, a *hexanitrosochloride*, and a *nitrosate*. The trinitrosochloride was further converted into a *dinitrosochloride mononitrolpiperidide*, a *trinitrolpiperidide*, a *dinitrosochloride mononitrolbenzylamide*, and a *trinitrolbenzylamide*. On hydrogenation, spinacene gave a saturated *hydrocarbon*, $C_{30}H_{62}$, b. p. 274—275°/18 mm., D_{20}^{20} 0·8172, n_D^{20} 1·4547.

For experimental details see the original. D. F. T.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. III. Chain Compounds and Sulphur. PRAFULLA CHANDRA RÂY (T., 1917, **111**, 101—109. Compare A., 1916, i, 246, 542).—As thiocarbamide, thioacetamide, and thiobenzamide are capable of reacting in a tautomeric form as iminomercaptans (Rây, T., 1914, **105**, 2159; A., 1916, i, 633), these compounds might be expected to react with mercuric nitrite; this anticipation has been realised, but the result is not quite as expected. Thus thiocarbamide and mercuric nitrite in aqueous solution yield a *substance*, $NH_2\cdot C(:NH)\cdot S(HgNO_2)<{}^{Hg}_{O}$, probably formed by elimination of a molecule of nitrogen trioxide from an additive compound of the primary product, $NH_2\cdot C(:NH)\cdot S\cdot HgNO_2$, with more mercuric nitrite. The former product is obtained only with certain precautions, the more usual product, which is formed exclusively when thioacetamide, thiobenzamide, and the thiocarbimides are submitted to the same reaction, being a compound, $(HgO,3SHgNO_2)_2$. This substance, to which the structure

$$Hg<\underset{\text{———————O———————}}{S(S\cdot HgNO_2)(HgNO_2)}>S(HgNO_2)$$
$$|$$
$$S(HgNO_2)<\underset{\text{———————O———————}}{S(S\cdot HgNO_2)(HgNO_2)}>Hg$$

is ascribed, reacts with methyl iodide, giving the disulphonium compound, Me_2S_2,HgI_2,MeI, and with ethyl iodide yielding *dimercuric di-iodosulphide*, $HgI\cdot S_2\cdot HgI$, together with a *compound*, $SEt\cdot S\cdot SEtI\cdot HgI$, and a compound, Et_2S_2,HgI_2,EtI.

For details the original should be consulted. D. F. T.

Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 17920, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 162).—Acetic anhydride is prepared by acting on an acetate with sulphuric oxide (which may or may not be mixed with chlorosulphonic acid) or with a compound of sulphuric oxide with an inorganic salt, for example, sodium chloride or sulphate. A diluent, such as acetic anhydride, is used, and the reaction mixture must be cooled initially to 0—5° if sulphuric oxide is employed directly

or to atmospheric temperature by water cooling if a compound of sulphuric oxide is used. Thus, sulphuric oxide (800 kilos.) is added fairly rapidly, with constant stirring, to powdered anhydrous sodium sulphate (1600 kilos.), and when combination is complete the mass is cooled and added to a mixture of powdered anhydrous sodium acetate (1640 kilos.) and acetic anhydride (1600 kilos.), the mixture being stirred and water-cooled. The temperature may subsequently be allowed to rise to 60—70° to complete the reaction. The acetic anhydride is distilled under diminished pressure. The product is of a high degree of purity and free from chlorine. H. W.

Isomerism of Erucic, Brassidic, and *iso*Erucic Acids. Results obtained by the Cryohydrate or Eutectic Method. V. L. MASCARELLI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 71—74. Compare A., 1915, i, 863, 937).—These acids have been subjected to conditions analogous to those employed in Biilmann's experiments (A., 1909, i, 155, 382), but in no case could transformation of one acid into either of the other two be observed. A few experiments have also been made on the lines of those carried out by Stobbe and Schönburg (A., 1914, i, 173) on the cinnamic acids, but none of the three acids undergoes change on protracted storage or on separation from solution in various solvents.

The method given by Sidgwick (T., 1915, **107**, 673), which had previously been suggested by Bruni (*Atti Accad. Sci. Padova*, 1910, **26**, 357), has also been applied to the elucidation of the relations between the erucic acids. The results obtained show that erucic and brassidic acids are truly isomeric, this conclusion being in complete accord with the results of the author's previous work and with the mode of formation of the one acid from the other. Erucic and *iso*erucic acids also represent a case of true isomerism, but brassidic and *iso*erucic acids are more probably to be regarded as two forms of one and the same compound, that is, as dimorphous. T. H. P.

Alkaline Earth Oxalates. W. ŒCHSNER DE CONINCK (*Ann. Chim. anal.*, 1917, **22**, 23—24. Compare A., 1916, i, 369).—When very dilute barium nitrate solution is mixed with a slight excess of dilute oxalic acid solution, a precipitate of the trihydrate of barium oxalate, $2BaC_2O_4,3H_2O$, forms gradually within a period of about four weeks. Under similar conditions, calcium yields a mixture of mono- and di-hydrates, the latter predominating. Strontium hydrogen oxalate is obtained as the trihydrate, $Sr(HC_2O_4)_2,3H_2O$, by treating concentrated strontium chloride solution with its own volume of concentrated hydrochloric acid and adding three volumes of saturated oxalic acid solution; this salt is decomposed by boiling water, with the formation of the normal salt, SrC_2O_4,H_2O. W. P. S.

Influence of Aminoacetic Acid and α-Aminopropionic Acid on the Action of Alkali on Dextrose. H. I. WATERMAN (*Chem. Weekblad*, 1917, **14**, 119—124).—Measurements of the

polarising power of dextrose solutions acted on by sodium hydroxide at 33° indicate that the presence of glycine or alanine retards the action. A. J. W.

Organic Double Compounds of the Bismuth Haloids. L. VANINO and F. MUSSGNUG (*Ber.*, 1917, **50**, 21—24).—The bismuth haloids form well-crystallised, yellow or red additive compounds with thiocarbamides of the general type $BiX_3,3CS(NR_2)_2$.

The yellow and red compounds of bismuth chloride with thiocarbamide, described by Hofmann and Gonder (A., 1904, i, 231), are of the same composition, $BiCl_3,3CS(NH_2)_2$. The yellow form melts at about 180° and the red at 186°, and the yellow substance changes into the red on drying. Other *compounds* obtained are as follows: $BiCl_3,3NH_2{\cdot}CS{\cdot}NHPh$, m. p. 157—158°;

$$BiCl_3,3NH_2{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me(o),$$

yellow prisms, m. p. 185°; $BiBr_3,3CS(NH_2)_2$, m. p. 193°; $BiI_3,3CS(NH_2)_2$, cinnabar-red, m. p. 164—165°.

Trimethylsulphonium iodide gives a reddish-yellow *compound*, $BiCl_3,SMe_3I$, m. p. 228°, and phenyl mercaptan forms the *compound*, $Bi(SPh)_3$, m. p. 98—99°.

Antimony trichloride combines with thiocarbamide to give a lemon-yellow *compound*, $SbCl_3,3CS(NH_2)_2$. J. C. W.

Preparation of Pharmaceutical Products containing Arsenic. SYNTHETIC PATENTS Co. (U.S. Pat., 1201692; from *J. Soc. Chem. Ind.*, 1917, **36**, 162—163).—Compounds containing the following groups are claimed: $RC\colon CR'As$, $RCX\colon CR'As$, $RCX\colon CR'AsO$, $CRX\colon CR'{\cdot}AsO(OH)_2$, $RCCl\colon CR'AsO(OH)_2$ (in which R or R′ is hydrogen or a hydrocarbon radicle and X is a halogen), and, in particular, the chloroarsinic acids produced by causing arsenic trichloride to combine with hydrocarbons of the acetylene series, treating the product with water to form the arsenoxide and oxidising the latter. Thus, Δ^{a}-heptinene (240 parts) is heated under reflux with arsenic trichloride (900 parts) for sixteen hours; excess of arsenic trichloride is removed by distillation in a vacuum, and the oily residue is dissolved in wet ether (3000 parts). Aniline is added as long as a precipitate forms, and the aniline hydrochloride is removed. The filtrate is washed with dilute hydrochloric acid, then with water until neutral to Congo-red, dried over sodium sulphate, and freed from ether in a vacuum. *Chloroheptinenearsen oxide* remains as a viscous, dark liquid, 44 parts of which are dissolved in acetone (400 parts) and treated with hydrogen peroxide (3%) until oxidation is complete. The solution is shaken with ether (500 parts), and the ethereal layer washed with dilute sodium hydroxide and water. The alkaline wash-water is acidified with hydrochloric acid and concentrated in a vacuum at 60—70° until the *chloroheptinenearsinic acid* crystallises. It is separated, washed with a little ether, decolorised with animal charcoal, and crystallised. It forms white, shining leaflets, readily soluble in water to a neutral solution, and is valuable in the treatment of anæmia, chlorosis, leucæmia, chorea, and skin diseases. H. W.

Preparation of Monoalkylated Aromatic Amines (*N*-Alkylarylamines). G. T. MORGAN (Brit. Pat., 102834; from *J. Soc. Chem. Ind.*, 1917, **36**, 207—208).—*N*-Alkylarylamines are prepared from aniline or naphthylamines or their homologues or simple substitution products (other than nitro-compounds) by treating the amine with an aliphatic aldehyde in the presence of a reducing agent in a medium not possessing a strongly acid character. The anhydroaldehyde–amine, or Schiff base, produced from the amine and aldehyde, is simultaneously reduced to the alkylaromatic amine. Thus, aniline (60 parts) and formaldehyde (40%, 66 parts) are added slowly and concurrently to a solution of sodium hydroxide (34%, D 1·37, 300 parts) containing zinc dust (90 parts) in suspension. The addition of the reagents should occupy about two hours, and the mixture should be well stirred and kept at 90°. The heating and stirring are continued for six hours longer, during which formaldehyde (40%, 40 parts) is slowly added. When the percentage of methylaniline has reached a maximum, the mixture is steam distilled, and the methylaniline isolated from the distillate in any of the usual ways. H. W.

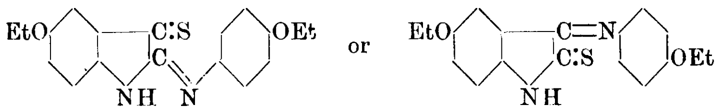
Electrolytic Preparation of Aromatic Amino-hydroxy-compounds. SOC. CHIM. IND., BASLE (Brit. Pat., 18081, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 129).—In the electrolytic reduction of aromatic nitro-compounds, the formation of aminohydroxy-compounds is favoured and that of amine reduced by the use of a cathode of two or more metals. The cathode is obtained either by use of a suitable alloy, the surface of which remains practically constant in composition during the reaction, or by making the cathode of one metal and placing the other, either as such or as salt, in the electrolyte, or by using an indifferent substance, such as carbon, and depositing the metal thereon during electrolysis. It is possible to reduce the amount of acid to very little more than that necessary to combine with the base which is formed. Details are given of the reduction of nitrobenzene, using a copper cathode with lead, or lead and arsenic, in the solution, and with a lead cathode with bismuth in the electrolyte. Other suitable combinations of metals are copper with mercury and copper with tin and arsenic. A plain lead cathode under these conditions would give *p*-aminophenol and aniline in the proportion of about 2 to 3, whilst this method gives them in the proportion of 5 or 6 to 1. H. W.

Certain Products of the Action of Formaldehyde and a Hydrogen Sulphite on Aromatic Amines and their Derivatives. I. ROBERTO LEPETIT (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 126—132).—Sodium *p*-phenetidinomethanesulphonate (nevralteine) (compare A., 1909, i, 569) decomposes and turns yellow at about 150°, sulphur dioxide, water, and aromatic vapours being emitted. The corresponding acid, which forms shining, white needles, first acid and then intensely sweet to the taste, begins to decompose at 70—75°, with liberation of sulphur dioxide, m. p.

146° (decomp.). Treatment of the free acid in aqueous alcoholic solution with an alcoholic solution of the equivalent quantity of an aromatic base yields the salt of the base. p-*Phenetidine* p-*phenetidinomethanesulphonate*,

$$OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3H,OEt\cdot C_6H_4\cdot NH_2,$$

thus obtained, forms shining, white lamellæ, m. p. 137° (decomp.). When heated above the melting point, either sodium or *p*-phenetidine *p*-phenetidinomethanesulphonate yields a compound, $C_{18}H_{18}O_2N_2S$, which forms lemon-yellow needles, m. p. 192—193°, and has the probable constitution



For derivatives of this class the name thioindamidines is suggested, the above compound being termed p-*phenetidinethioindamidine*-p-*phenetidine.*

Sodium p-*anisidinomethanesulphonate*,

$$OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3Na,H_2O,$$

obtained from *p*-anisidine, formaldehyde, and sodium hydrogen sulphite, forms shining, white lamellæ; *sodium* p-*chloroanilinomethanesulphonate*, $C_6H_4Cl\cdot NH\cdot CH_2\cdot SO_3Na,H_2O$, shining, white scales with a greasy feel; sodium *p*-toluidinomethanesulphonate (compare Bucherer and Schwalbe, A., 1906, i, 828) crystallises with $1H_2O$; *sodium* p-*acetylaminoanilinomethanesulphonate*,

$$NHAc\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3Na,$$

forms shining, white crystals, and the corresponding *acid*, crystals, m. p. 153—154° (decomp.).

Sodium azobenzeneaminomethanesulphonate,

$$NPh:N\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3Na,H_2O,$$

obtained from aminoazobenzene, formaldehyde, and sodium hydrogen sulphite, forms shining, orange chips, and the corresponding acid, microscopic, purple crystals. This compound and the analogous one obtained from aminoazotoluene (m. p. 100°), behave normally towards potassium cyanide, giving the corresponding nitriles, from which the amides and thioamides may be prepared.

T. H. P.

Action of Alkalis and Acids on Sodium *p*-Phenetidinomethanesulphonate. II. ROBERTO LEPETIT (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 172—174. Compare preceding abstract). —The action of dilute sodium hydroxide solution on sodium *p*-phenetidinomethanesulphonate has been investigated with the object of obtaining anhydroformophenetidine, $OEt\cdot C_6H_4\cdot N:CH_2$, but it is found that the action proceeds quantitatively according to the equation: $2OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3Na + 2NaOH = (OEt\cdot C_6H_4\cdot NH)_2CH_2 + CH_2O + H_2O + 2Na_2SO_3$. Other arylaminomethanesulphonates undergo the same reaction, which represents a good general method for preparing imides. If pure methanesulphonates are used, the di-imides are obtained in a pure state,

but on recrystallisation the melting point becomes lowered, owing to decomposition.

The action of boiling dilute hydrochloric acid on *p*-phenetidinomethanesulphonic acid yields *p*-phenetidine hydrochloride and a substance which crystallises in pale yellow, shining needles, and is the hydrochloride of a sulphur-free *base*, $C_{18}H_{20}O_2N_2$, m. p. 140°, exhibiting anæsthetic properties. When *p*-phenetidinomethanesulphonic acid is boiled with water alone, sulphur dioxide and formaldehyde are evolved, the residual product being the p-*phenetidinomethanesulphonate* of the above base,

$$C_{18}H_{20}O_2N_2,OEt\cdot C_6H_4\cdot NH\cdot CH_2\cdot SO_3H,$$

which crystallises in white needles, m. p. 160—161°, and exerts a pronounced and moderately persistent anæsthetic action.

T. H. P.

Preparation of Auromercaptobenzenes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat., 1207284, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 163).—Auromercaptobenzenes of the general formula X·S·Au (where X is any benzene nucleus) are obtained by the action of double gold chlorides on mercaptobenzenes. They are yellow solids. The *sodium* salt of 4-amino-2-auromercaptobenzene-1-carboxylic acid is a yellow powder, readily soluble in water, insoluble in organic solvents. H. W.

Mixed Chains containing Carbamide, Methylenediamine, and Amino-acid Residues. THEODOR CURTIUS (*J. pr. Chem.*, 1916, [ii], **94**, 85—134).—During his researches on acid azides, the author has obtained compounds which contain carbamide, methylenediamine, and glycine residues, for example, the substance of the formula

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$$

(A., 1904, i, 888). When such products are hydrolysed, they yield amino-acids, ammonia, amines, carbon dioxide, and formaldehyde, the above substance, for example, giving $NH_2Ph + 2CO_2 + 2NH_2\cdot CH_2\cdot CO_2H + 2NH_3 + H\cdot CHO + EtOH$. This is of considerable interest in view of the fact that the production of ammonia and carbon dioxide is also observed in the hydrolysis of proteins, and therefore the author has set out to synthesise complex compounds of the above type.

Two discoveries render this task fairly easy of accomplishment. The first is that carbimides are readily obtained by the decomposition of acid azides in indifferent media (Schroeter, A., 1909, i, 617; Stoermer, *ibid.*, 785; Curtius, A., 1913, i, 897), and the other that carbimides react easily with the esters of amino-acids (Fischer, A., 1906, i, 324) to form esters of carbamido-acids. If these are converted through the hydrazides and azides into the corresponding carbimides, condensation with further amino-acids is possible again, and so complex substances of the desired type can be built up. Some examples are now given.

[With ADRIEN LAURENT.]—I. *Combination of Hippenylcarbimide with Ethyl Glycine.*

Hippuroylazide is converted into hippenylcarbimide (benzoylaminomethylcarbimide) (*ibid.*), and this is mixed with ethyl glycine, when *ethyl hippenylcarbamidoacetate* (*benzoylaminomethylcarbamidoacetate*) is formed, in white needles, m. p. 149—155°. The corresponding *acethydrazide*,

$$NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is obtained by boiling the ester with hydrazine hydrate, in microscopic needles, m. p. 206—207°. It yields benzoic acid, ammonia, formaldehyde, carbon dioxide, glycine, and hydrazine on hydrolysis, and these can be identified by suitable means. It also forms a *benzylidene* compound, m. p. 236°, but the corresponding azide has not been obtained pure.

[With WILLIAM F. ZIMMERLI.]—II. *Combination of Hippenylcarbimide and* p-*Bromohippenylcarbimide with Esters of* l-*Aspartic Acid.*

Methyl *l*-aspartate reacts with the above carbimide to form *methyl hippenylcarbamidosuccinate*,

$$NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO_2Me)\cdot CH_2\cdot CO_2Me,$$

which crystallises in small granules, m. p. 153°. The corresponding *ethyl* ester forms small, white needles, m. p. 150°, and the free *acid* crystallises in rhombohedra, m. p. 159°, decomposes sodium carbonate, and gives an *ammonium* salt, m. p. 186° (decomp.), and a pale green *copper* salt. The *dihydrazide* forms microcrystalline granules, m. p. 102°, and yields a *dibenzylidene* compound, m. p. 212°, a *disalicylidene* compound, m. p. 206°, a *di*iso*propylidene* compound, m. p. 194°, and a *dibenzoyl* derivative, m. p. 207° (decomp.), when treated with the appropriate agents. The dihydrazide loses hydrazine when boiled with water, and changes into N-*aminohippenylcarbamidosuccinimide*,

$$\begin{array}{l} NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH-CO \\ \qquad\qquad\qquad\qquad\qquad\quad\; | \\ \qquad\qquad\qquad\qquad\qquad\; CH_2\cdot CO \end{array}\!\!>N\cdot NH_2,$$

m. p. 144°, which also forms a *benzylidene* compound, m. p. 221°, which is acid to litmus.

The dihydrazide is readily converted into *hippenylcarbamidosuccinyldiazide*,

$$NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO\cdot N_3)\cdot CH_2\cdot CO\cdot N_3,$$

by the action of nitrous acid. This does not keep for more than a day or so, as it loses nitrogen easily, although without violence, and changes into the *dicarbimide*, m. p. 192°. For some of the reactions in which the carbimide is involved, it is therefore possible to use the azide itself. Thus, alcohol yields the *diurethane*,

$$NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(NH\cdot CO_2Et)\cdot CH_2\cdot NH\cdot CO_2Et,$$

m. p. 172°; aniline forms the *dicarbamanilide*,

$$NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(NH\cdot CO\cdot NHPh)\cdot CH_2\cdot NH\cdot CO\cdot NHPh,$$

m. p. 192°; *p*-toluidine gives an analogous *compound*, m. p. 195°. The dicarbimide also reacts with ethyl *l*-aspartate to form the *compound*,

$$\begin{array}{l} NHBz\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH\cdot NH\cdot CO\cdot NH\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et' \end{array}$$

m. p. 124°. The corresponding tetrahydrazide and azide have been cursorily examined.

p-Bromohippenylcarbimide (*ibid.*) reacts with ethyl *l*-aspartate to form *ethyl* p-*bromohippenylcarbamidosuccinate*, slender needles, m. p. 162°, and this may be converted into the *dihydrazide*, m. p. 197°, and diazide in the usual way.

[With GEORG PETRIDIS.]—III. *Combination of Hippurylaminomethylcarbimide with Amides and Glycine Esters.*

Hippurylaminomethylcarbimide,

$$NHBz\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot N\colon CO,$$

white leaflets, m. p. 122° (decomp.), is obtained from the corresponding azide (A., 1904, i, 833). New details are given in connexion with the preparation of this substance, including the statement that the necessary ethyl hippurylglycine can be obtained by benzoylating ethyl glycylglycine.

When boiled with water, this carbimide is transformed into *dihippurylaminomethylcarbamide* [" *diglycylhippenylcarbamide* "], $CO(NH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NHBz)_2$, a white powder, m. p. 250° (decomp.), whilst alcohol converts it into ethyl hippurylaminomethylcarbamate, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$, m. p. 202° (*ibid.*). It also reacts with benzamide to form *benzoylhippurylaminomethylcarbamide*, needles, m. p. 224°, and with acetamide to yield the corresponding *acetyl* compound,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NHAc,$$

m. p. 179—180°.

The carbimide also reacts with ethyl glycine, yielding *ethyl hippurylaminomethylcarbamidoacetate*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

small, white needles, m. p. 179—180° The corresponding free *acid* crystallises in slender needles, m. p. 204·5°, and forms an *ammonium* salt, m. p. 216°, and a *silver* salt, m. p. 191°, whilst the corresponding *amide*, m. p. 196°, *hydrazide*, silvery leaflets, m. p. 239° (*benzylidene* compound, m. p. 254°), and *azide*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_3,$$

white needles, m. p. 113—114°, have also been obtained.

[*Supplementary.*]—I. With WILLIAM F. ZIMMERLI.—*Attempts to prepare Acetylaminoacetazide.*—Ethyl acetylaminoacetate is conveniently obtained by warming together ethyl glycine hydrochloride (1 mol.), anhydrous sodium acetate (a little more than 1 mol.), copper sulphate (about 0·1 mol.), and acetic anhydride (2 mols.), or by the action of acetyl chloride (compare Radenhausen, A., 1896, i, 137). The hydrazide is obtained from this by means of cold hydrazine hydrate (*ibid.*; *hydrochloride*, m. p. 177°). This reacts with acetone to form the iso*propylidene* compound,

$$NHAc\cdot CH_2\cdot CO\cdot NH\cdot N\colon CMe_2,$$

m. p. 144°, but all attempts to convert it into the azide by means of nitrous acid resulted in the formation of diacetylglycylhydrazide, $N_2H_2(CO\cdot CH_2\cdot NHAc)_2$, large leaflets, m. p. 259—260° (*ibid.*).

II. With GEORG PETRIDIS.—*Hydrazide and Azide of* p-*Nitrohippuric and* p-*Nitrohippurylaminoacetic Acids* (compare A., 1914, i, 871).—Ethyl *p*-nitrohippurate, m. p. 142° (Klages and Haack,

A., 1903, i, 560), and *ethyl* o-*nitrohippurate*, white needles, m. p. 81°, are readily obtained by the action of the nitrobenzoyl chlorides on ethyl glycine. p-*Nitrohippurhydrazide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

forms slender, yellow needles, m. p. 203·5°, and yields a *benzylidene* compound, a yellow powder, m. p. 216°, and an iso*propylidene* compound, white leaflets, m. p. 211°. p-*Nitrohuppurazide* is a fine, yellow powder, m. p. 70—72° (decomp.), which decomposes within a few days.

Ethyl p-*nitrohippurylaminoacetate*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

yellow needles, m. p. 172—173°, is obtained by acylating glycylglycine ester. The corresponding *hydrazide* crystallises in yellow leaflets, m. p. 249°, forms a *benzylidene* compound, m. p. 263°, and gives rise to the *azide*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_3$, a voluminous, yellow powder, m. p. 91—92° (decomp.).

III. With WILLIAM F. ZIMMERLI.—*Interaction of Hippenylcarbimide and Hydrochlorides of Amino-acid Esters.*—If, instead of using the free esters in the above reactions, hippenylcarbimide is treated with the hydrochlorides of methyl *l*-aspartate or ethyl glycine, the same abnormal *compound*, m. p. 215°, 13·1% N, is obtained. J. C. W.

Ester Condensations with Naphthylacetic Esters. WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1916, **49**, 2820—2830).—The esters of α- and β-naphthylacetic acids condense with ethyl formate under the influence of sodium to give formylnaphthylacetic esters. These exist in enol ("α") and aldo ("β") modifications.

For the preparation of the naphthylacetic esters, the methylnaphthalenes are vigorously treated with bromine, the naphthylmethyl bromides are converted into nitriles, and warm alcoholic solutions of these are submitted to a brisk stream of hydrogen chloride. *Ethyl naphthyl*-1-*acetate* is a colourless oil, b. p. 177—179°/13 mm., and *ethyl naphthyl*-2-*acetate* has m. p. 31—32°, b. p. 186—187°/14 mm.

Enolic ("α") *ethyl formylnaphthyl*-1-*acetate*,

$$C_{10}H_7\cdot C(CO_2Et)\colon CH\cdot OH,$$

crystallises from alcohol in glistening leaflets, m. p. 53—55°, gives a deep reddish-violet colour with ferric chloride, will keep for months in a desiccator or closed vessel, and combines with phenylcarbimide to form the *compound*,

$$C_{10}H_7\cdot C(CO_2Et)\colon CH\cdot O\cdot CO\cdot NHPh,$$

m. p. 79—80°. The β-*modification* crystallises from chloroform mixed with light petroleum in stellar aggregates of needles, m. p. 115—118°, does not react with phenylcarbimide, and is fairly stable at the ordinary temperature if contact with traces of alkali is avoided. Alcoholic solutions of the α-form quickly give a precipitate of the *copper* salt, $Cu(C_{15}H_{13}O_3)_2,EtOH$ (flat, green needles, m. p. 118—120°, or 192—194° when free from alcohol), when treated with copper acetate; the β-modification reacts slowly, apparently

after isomerisation. Solutions of the potassium salt give precipitates of the β-modification when added to sulphuric acid, copper sulphate, or ferric chloride solutions, but if treated with a current of carbon dioxide, or if these salts are added to the solution, then the free ester or the copper or ferric salts of the α-form are obtained.

The α-form of *ethyl formylnaphthyl-2-acetate*, m. p. 50—51°, is best obtained by converting the crude mixture of the two modifications into the *copper* salt, m. p. 186—188°, and decomposing this by dilute sulphuric acid. It gives a deep bluish-violet colour with ferric chloride. The *β-modification*, m. p. 86—87°, is formed when the solution of the potassium salt is stirred into 30% sulphuric acid. It changes more readily into the α-form than the corresponding ester of formylnaphthyl-1-acetic acid. J. C. W.

The Nitration of 2-Acetylamino-3 : 4-dimethoxybenzoic Acid and 3-Acetylaminoveratrole. CHARLES STANLEY GIBSON, JOHN LIONEL SIMONSEN, and MADYAR GOPALA RAU (T., 1917, **111**, 69—85).—On nitration of 2-acetylamino-3 : 4-dimethoxybenzoic acid, 6-*nitro-2-acetylamino-3 : 4-dimethoxybenzoic acid*,

$$NO_2 \cdot C_6H(OMe)_2(NHAc) \cdot CO_2H,$$

was obtained as sole product; this substance, when cautiously hydrolysed with sulphuric acid, gave 6-*nitro-2-amino-3 : 4-dimethoxybenzoic acid*, $NO_2 \cdot C_6H(OMe)_2(NH_2) \cdot CO_2H$, but when heated with somewhat diluted hydrochloric acid was converted into 5-*nitro-3-aminoveratrole*, $NO_2 \cdot C_6H_2(OMe)_2 \cdot NH_2$, with loss of carbon dioxide. 5-Nitro-3-aminoveratrole was also obtainable in the form of its acetyl derivative by the nitration of 3-acetylaminoveratrole (see below).

By means of the diazo-reaction, 5-nitro-3-aminoveratrole was converted through the *nitrile*, $NO_2 \cdot C_6H_2(OMe)_2 \cdot CN$, into 5-nitro-2 : 3-dimethoxybenzoic acid, which has already been described (Cain and Simonsen, T., 1914, **105**, 159). 6-Nitro-2 : 3-dimethoxybenzoic acid, whatever its method of preparation, has m. p. 185—186° (Perkin and Robinson, T., 1914, **105**, 2390, gave 178·5°; compare also Wegscheider and Klemenc, A., 1910, i, 670).

In the nitration of 2-acetylamino-3 : 4-dimethoxybenzoic acid, especially under slightly modified conditions, there was also obtained 4 : 5-*dinitro-3-acetylaminoveratrole*,

$$NHAc \cdot C_6H(NO_2)_2(OMe)_2,$$

which is soluble in aqueous alkalis; this was also produced, together with 5 : 6-*dinitro-3-acetylaminoveratrole*, by the nitration of 3-*acetylaminoveratrole* or of 5-*nitro-3-acetylaminoveratrole*, which were prepared from 3-*aminoveratrole* by acetylation or successive acetylation and nitration respectively. When heated with sulphuric acid, the 4 : 5-dinitro-3-acetylaminoveratrole was converted into 4 : 5-*dinitro-3-aminoveratrole*, $NH_2 \cdot C_6H(NO_2)_2(OMe)_2$; in a similar manner, the 5 : 6-dinitro-3-acetylamino-isomeride yielded 5 : 6-dinitro-3-aminoveratrole.

When 4 : 5-dinitro-3-aminoveratrole was diazotised in alcoholic

solution, the product obtained was 4 : 5-*dinitroveratrole*,

$$C_6H_2(NO_2)_2(OMe)_2;$$

but on diazotisation in acetic acid containing a little sulphuric acid, scission of a methyl group occurred, the product of coupling with β-naphthol being 4 : 5-*dinitro-2-hydroxy-1-methoxy-3-azo-β-naphthol*, $OH\cdot C_6H(OMe)(NO_2)_2\cdot N_2\cdot C_{10}H_6\cdot OH$; somewhat similarly, on heating the solution obtained by diazotising in a mixture of acetic and hydrochloric acids, 4-*chloro-5-nitroguaiacol*,

$$NO_2\cdot C_6H_2Cl(OH)\cdot OMe,$$

was formed. By diazotisation in alcoholic solution, 5 : 6-dinitro-3-aminoveratrole was converted into 3 : 4-*dinitroveratrole*, which was accompanied by a small quantity of a phenolic *substance*.

[With J. E. Purvis.]—On account of the solubility of 4 : 5-dinitro-3-acetylaminoveratrole in alkali to a yellow solution, whereas the 5 : 6-dinitro-isomeride is insoluble, the absorption spectra of these substances have been examined, the results indicating that the solubility in the former case is not due to any marked constitutional change.

For details, the original paper should be consulted. D. F. T.

Preparation of Seleno-phthaleins and their Halogen Derivatives. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 295253, addition to D.R.-P., 290540, 291883; from *J. Soc. Chem. Ind.*, 1917, **36**, 211).—In place of the phthalins specified in the previous patents (A., 1916, i, 560, 728), their *O*-acetyl compounds or *O*-acetyl compounds of phthaleins are used in indifferent solvents. The products are different from those obtained by the action of selenium on fluoresceins in aqueous alkaline solution in accordance with D.R.-P., 279549 (compare A., 1915, i, 409). H. W.

Action of Oxalyl Chloride on Ethers of the Naphthols. M. Giua (*Gazzetta*, 1917, **47**, i, 51—57).—The action of oxalyl chloride on α-naphthyl methyl ether in light petroleum solution and in presence of aluminium chloride yields: (1) mainly 4 : 4′-*dimethoxydi-α-naphthyl diketone*,

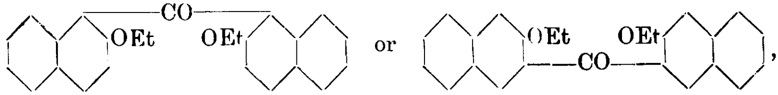
$$OMe\cdot C_{10}H_6\cdot CO\cdot CO\cdot C_{10}H_6\cdot OMe,$$

which forms pale yellow needles, m. p. 230—231°, and gives a red coloration with concentrated sulphuric acid; (2) a small proportion of 4 : 4′-*dimethoxydi-α-naphthyl ketone*,

$$OMe\cdot C_{10}H_6\cdot CO\cdot C_{10}H_6\cdot OMe,$$

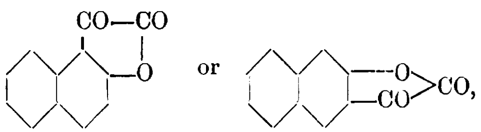
which forms shining, white plates, m. p. 142°, and gives a yellowish-red coloration with concentrated sulphuric acid.

The same reaction with β-naphthyl ethyl ether in carbon disulphide yields: (1) the *diethoxydinaphthyl ketone*,



which forms small, white prisms, m. p. 184°, and gives a pale yellow

coloration with concentrated sulphuric acid; (2) the *lactone* of a *hydroxynaphthylglyoxylic acid* (annexed formulæ), which crystallises in orange-yellow needles, m. p. 178° (decomp.), and gives a carmine coloration with concentrated sulphuric acid. T. H. P.



Coloured Organic Molecular Compounds. PAUL PFEIFFER [with W. JOWLEFF, PH. FISCHER, P. MONTI, and H. MULLY] (*Annalen*, 1916, **412**, 253—335. Compare A., 1914, i, 551).—It has already been indicated (*loc. cit.*) that the most important groups of coloured organic molecular compounds are probably closely related in type with the halochromic compounds of the aldehydes, ketones, and acids. By analogy, therefore, it would be expected that nitro-compounds should be capable of forming halochromic compounds with metallic salts and acids in the same manner as do ketones, and such compounds have now been observed with unsaturated nitro-compounds, such as the nitrostilbenes and nitrostyrenes. The colour of all these molecular compounds is referred to the one-sided saturation effected at the double linking of the group by which attachment is made; thus, in the ketones and nitro-compounds, the uneven distribution of the saturation must leave a certain amount of free valency at the carbon and nitrogen atoms respectively, as may be represented by the formulæ $R_2\underset{\downarrow}{C}{:}O \ldots A$ and $R\underset{\downarrow}{N}O_2 \ldots A$, where the arrow represents the free valency and A the molecule of the second constituent; on account of the degree of unsaturation thus produced in it, the carbon or nitrogen atom assumes the character of a chromophore. In some of the types of molecular compounds, such as the quinhydrones, the second molecule probably contributes considerably to the colour of the compound by supplying a second chromophoric atom, thus, $R_2\underset{\downarrow}{C}{:}O \ldots \underset{\downarrow}{C}{:}C$.

The formulation of the coloured additive compounds of phenols with quinones as $O{:}C_6H_4{:}O \ldots C_6H_4(OH)_2$ and

$$OH{\cdot}C_6H_5 \ldots O{:}C_6H_4{:}O \ldots C_6H_5{\cdot}OH,$$

is confirmed by the fact that quinones can form with aromatic hydrocarbons coloured additive compounds resembling the quinhydrones in stability; the hydroxyl or amino-radicle is therefore not essential to the formation of "quinhydrone" compounds, neither, indeed, is hydrogen itself, because hexamethylbenzene is capable of yielding coloured additive compounds with quinones. It is therefore necessary to assume that the power of forming quinhydrone compounds with quinones is due to the benzene nucleus of the second reagent, and the fact that hexahydrodurene does not produce any colour reaction with quinones, whilst durene itself does, is in agreement with this assumption. Terpenes and un-

saturated compounds, such as dimethylbutadiene, dissolve quinones, giving more or less deeply coloured solutions, and this effect is doubtless to be attributed to the unsaturated condition, in which these hydrocarbons resemble the benzene hydrocarbons.

Not only *p*-quinones, but also *o*-quinones, such as phenanthraquinone, are able to form additive compounds with benzene hydrocarbons, for example, hexamethylbenzene. It is found that with the quinhydrones, methyl groups present in the quinonoid constituent have a hypsochromic effect on the colour, whilst methyl groups in the benzenoid component exert a bathochromic influence; the effect of methoxyl and hydroxyl groups is similar to that of the methyl group, but halogen atoms, on the contrary, exert a bathochromic effect when in the quinonoid nucleus and a hypsochromic effect in the benzenoid component.

The constitution of the compounds of hydrocarbons with nitro-compounds is likewise explained as due to attachment between the unsaturated nitro-group and the unsaturated hydrocarbon nucleus (compare Werner, A., 1910, i, 20). Accordingly, the analogy between compounds of the type $R\cdot NO_2 \ldots C_6H_6$ and of the type $R_2CO \ldots C_6H_6$ is a close one. *s*-Trinitrobenzene is especially well adapted to the formation of additive compounds with aromatic hydrocarbons, and in view of this result, the compounds of these hydrocarbons with picric acid are not to be regarded as "picrates," but should be represented by $OH\cdot C_6H_2(NO_2)_3 \ldots C_nH_m$, that is, as the hydroxyl derivatives of the corresponding trinitrobenzene compounds. Once more it is found that the methyl groups in the benzenoid component are bathochromic in influence, but are hypsochromic in the nitro-constituent. By analogy with the hydrocarbon derivatives, and because of the regularity of the effects produced on introducing the various substituents, the additive compounds of the nitro-compounds with phenols and amines must be represented $R\cdot NO_2 \ldots C_6H_5\cdot OH$ and $R\cdot NO_2 \ldots C_6H_5\cdot NH_2$.

The analogy between nitro-compounds and ketones in the formation of molecular compounds leads to the expectation of additive compounds between nitro-compounds and metallic salts or acids; nitro-compounds containing ethylenic linkings exhibit more pronounced halochromic phenomena than do ordinary aromatic nitro-compounds, and their methyl or methoxy-derivatives are especially noteworthy in this respect. Only in relatively few cases have the solid halochromic compounds been isolated, the formation being in most cases assumed from the colour of the solution of the substance, for example, in acetic acid or trichloroacetic acid.

The stannic chloride additive compounds of the ketones are represented as of the structure $SnCl_4{<}\begin{matrix}O\colon CRR'\\ O\colon CRR'\end{matrix}$, and the perchloric acid derivatives (compare Hofmann and others, A., 1910, i, 105, 168, 187, 370, 818), which also possess equimolecular constitution, are also regarded as containing the acid molecule linked to the ketone molecule, only through the oxygen atom, thus,

$$RR'C\colon O \ldots HClO_4.$$

With other acids, there is a tendency for the ketone to bind more

than a molecular proportion of acid, and it is believed that in these cases the constitution is still the same and that the acid has reacted in a polymerised condition. For the purpose of examining the halochromy with these compounds, the stannic chloride compounds are compared in the crystalline condition, whilst the perchlorates, on account of their tendency to exhibit surface lustre, are compared in solution. The interposition of ethylene linkings between the benzene nucleus and the carbonyl group deepens the colour of the additive compounds. A colour comparison of the stannic chloride and sulphuric acid additive compounds of hydroxybenzophenone and hydroxyxanthone with the alkaline solutions of these substances reveals a notable similarity, suggesting that the colour of the alkali salts is due to halochromy, and that the constitution of these salts should be represented $C_6H_4{<}^{O-M}_{CR:O}$, where M is the metallic atom.

The following *additive* compounds are described: *chloro*-p-*benzoquinone—hexamethylbenzene*, $C_6H_3O_2Cl,C_6Me_6$, orange-coloured needles, m. p. 99—103°; 2:5-*dichloro*-p-*benzoquinone—durene*, $C_6H_2O_2Cl_2,2C_6H_2Me_4$, orange-yellow tablets, m. p. 82—86°; 2:5-*dichloro*-p-*benzoquinone—hexamethylbenzene*,

$$C_6H_2O_2Cl_2,C_6Me_6,$$

red needles, m. p. 132—136°; *tetrachloro*-p-*benzoquinone—hexamethylbenzene*, $C_6O_2Cl_4,C_6Me_6$, violet-brown needles, m. p. 198—202°; *tetrabromo*-p-*benzoquinone—hexamethylbenzene*,

$$C_6O_2Br_4,C_6Me_6,$$

deep violet-brown needles, m. p. 198—203°; *tetrachloro*-o-*benzoquinone—benzene*, $C_6O_2Cl_4,3C_6H_6$, deep red crystals, m. p. 37—42°; *tetrachloro*-o-*benzoquinone—toluene*, $C_6O_2Cl_4,C_6H_5Me$, deep red needles, m. p. 45—50°; *tetrachloro*-o-*benzoquinone*—p-*xylene*,

$$C_6O_2Cl_4,C_6H_4Me_2,$$

deep red prisms, m. p. near 83°; *tetrachloro*-o-*benzoquinone—hexamethylbenzene*, $C_6O_2Cl_4,C_6Me_6$, greenish-black needles, m. p. 140—143°; *phenanthraquinone—hexamethylbenzene*,

$$C_{14}H_8O_2,C_6Me_6,$$

orange needles, m. p. 160—163°.

s-*Trinitrobenzene—toluene*, $C_6H_3(NO_2)_3,C_6H_5Me$, very pale yellow needles; s-*trinitrobenzene—xylene*, $C_6H_3(NO_2)_3,C_6H_4Me_2$, greenish-yellow needles; s-*trinitrobenzene—durene*, $C_6H_3(NO_2)_3,C_6H_2Me_4$, greenish-yellow leaflets, m. p. 92—98; s-*trinitrobenzene—hexamethylbenzene*, yellow needles, m. p. 174—175°; s-*trinitrobenzene—stilbene*, $2C_6H_3(NO_2)_3,C_2H_2Ph_2$, golden-yellow needles, m. p. indistinct at 107—110°; s-*trinitrobenzene—hexamethylstilbene*, cinnabar-red prisms, m. p. 145—147°; s-*trinitrobenzene*—pp′-*dimethoxystilbene*, $2C_6H_3(NO_2)_3,C_2H_2(C_6H_4{\cdot}OMe)_2$, red needles, m. p. 145—155° (decomp.); 2:4-*dinitrodeoxybenzoin—aniline*,

$$COPh{\cdot}CH_2{\cdot}C_6H_3(NO_2)_2,NH_2Ph,$$

golden-yellow leaflets, m. p. near 91°; 2:4-*dinitro*-4′-*methyldeoxybenzoin—aniline*, $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(NO_2)_2,NH_2Ph$, yellow, leafy needles, m. p. 68°; 2:4-*dinitro*-4′-*methoxydeoxybenzoin—aniline*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(NO_2)_2,NH_2Ph$, yellow, leafy

needles, m. p. near 87°; 2:4:6-*trinitrostilbene—aniline*,

$CHPh{:}CH{\cdot}C_6H_2(NO_2)_3,NH_2Ph$,

orange-red leaflets, m. p. 103—105°; 2:4:6-*trinitrostilbene—dimethylaniline*, $CHPh{:}CH{\cdot}C_6H_2(NO_2)_3,NPhMe_2$, violet-brown leaflets, m. p. near 120°; 2:4:6-*trinitrostilbene*—o-*toluidine*, $CHPh{:}CH{\cdot}C_6H_2(NO_2)_3,C_6H_4Me{\cdot}NH_2$, red leaflets, m. p. near 120°. Many of the above compounds gradually decompose in the atmosphere, losing their volatile constituent.

The dinitrodeoxybenzoin (compare Borsche, A., 1912, i, 652) used above was also converted into its *oxime*, yellow needles, m. p. 137—139°; the 2:4-dinitrophenylacetyl chloride used in its preparation gave a corresponding *anilide*, $C_6H_3(NO_2)_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, yellow needles, m. p. 181—182°, and a *phenylhydrazide*, yellow needles, m. p. 174—176°. 2:4-*Dinitro-4′-methyldeoxybenzoin*, brownish-yellow needles, m. p. 135—136°, or less stable yellow leaflets, m. p. 95—96°, was prepared by the Friedel-Crafts' reaction with 2:4-dinitrophenylacetyl chloride and toluene in carbon disulphide, whilst 2:4-*dinitro-4′-methoxydeoxybenzoin*, yellow needles, m. p. 101—103°, was obtained in a similar manner, using anisole in place of toluene.

p-Anisyl styryl ketone in benzene solution with stannic chloride gave an *additive* compound,

$SnCl_4,C_6H_6,2CHPh{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$,

yellow crystals, m. p. near 105°. *Phenyl* o-*methoxystyryl ketone*, very pale yellow needles, m. p. 64—65°, prepared by the methylation of the corresponding hydroxyl compound, yielded an *additive* compound, $SnCl_4,2OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$, a red, crystalline powder, m. p. near 135—136°; in the preparation of the parent ketone by the condensation of anisaldehyde and acetophenone, o-*anisylidenediacetophenone*, $OMe{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}COPh)_2$, colourless needles, m. p. 113—114°, was also obtained.

Phenyl m-*methoxystyryl ketone*, pale yellow leaflets, m. p. 64°, obtained by the methylation of the corresponding hydroxy-compound and also by the direct condensation of *m*-methoxybenzaldehyde with acetophenone, formed the additive compound, $SnCl_4,2OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$, compact, yellow crystals, m. p. 100—110°. Phenyl *p*-methoxystyryl ketone gave an orange-red, crystalline *additive* compound of the same composition, m. p. 105—110°. Styryl *p*-methoxystyryl ketone gave an *additive* compound, $SnCl_4,CHPh{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$, a red, crystalline powder, m. p. near 172°. Di-*o*-methoxydistyryl ketone yielded from benzene solution an additive compound,

$SnCl_4,2CO(CH{:}CH{\cdot}C_6H_4{\cdot}OMe)_2,C_6H_6$,

orange-red crystals, m. p. 180°; the *meta* and *para* isomerides both gave additive compounds of the composition

$SnCl_4,2CO(CH{:}CH{\cdot}C_6H_4{\cdot}OMe)_2$,

orange-yellow crystals, m. p. near 170°, and a crystalline, black powder respectively. Dimethylenedioxydistyryl ketone yielded the *compound*, $SnCl_4,2CO(CH{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2)_2$, as a black precipitate from benzene solution. Styryl cinnamylidenemethyl ketone gave the *compound*, $SnCl_4,2CHPh{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CHPh$, copper-red leaflets, m. p. near 171°.

The following *additive* compounds with perchloric acid were prepared: with *p*-methoxybenzophenone, $COPh·C_6H_4·OMe,HClO_4$, yellowish-brown crystals; with phenyl styryl ketone,

$$COPh·CH:CH·C_6H_5,HClO_4,$$

yellow crystals, decomp. at 92—96°; with *p*-anisyl styryl ketone, $OMe·C_6H_4·CO·CH:CHPh,HClO_4$, orange-yellow crystals, m. p. 63—78°; with phenyl *p*-methoxystyryl ketone,

$$C_6H_5·CO·CH:CH·C_6H_4·OMe,HClO_4,$$

orange-red crystals with a blue glance, m. p. 103—107°; with styryl *p*-methoxystyryl ketone,

$$C_6H_5·CH:CH·CO·CH:CH·C_6H_4·OMe,HClO_4,$$

violet needles with a blue glance, m. p. 123—125°; with *pp'*-dimethoxydistyryl ketone, $CO(CH:CH·C_6H_4·OMe)_2,HClO_4$, violet-black crystals with green glance, decomp. at 160—162°; *oo'*-dimethoxydistyryl ketone, violet, crystalline powder with green glance; with styryl cinnamylidenemethyl ketone,

$$CHPh:CH·CH:CH·CO·CH:CHPh,HClO_4,$$

red needles with a faint green lustre, m. p. 156—163° (decomp.); with styryl *p*-methoxycinnamylidenemethyl ketone,

$$OMe·C_6H_4·CH:CH·CH:CH·CO·CH:CHPh,HClO_4,$$

steel-blue needles with a feeble green lustre, m. p. 133—147° (decomp.); with styryl *m*-methoxycinnamylidenemethyl ketone, a product of the same composition, violet-black crystals with green lustre, m. p. 155—157° (decomp.); with *p*-methoxystyryl *p*-methoxycinnamylidenemethyl ketone,

$$OMe·C_6H_4·CH:CH·CH:CH·CO·CH:CH·C_6H_4·OMe,HClO_4,$$

deep bluish-violet needles with green glance; with styryl methylenedioxycinnamylidenemethyl ketone,

$$CH_2:O_2:C_6H_3·CH:CH·CH:CH·CO·CH:CHPh,HClO_4,$$

blackish-violet needles with green glance, m. p. 138—151°; with dicinnamylideneacetone, $CO(CH:CH·CH:CHPh)_2.HClO_4$, bluish-violet needles with blue glance, decomp. 130—148°; with *pp'*-dimethoxydicinnamylideneacetone,

$$CO(CH:CH·CH:CH·C_6H_4·OMe)_2,HClO_4,$$

indigo-blue needles with green lustre, decomp. near 150°.

For the production of the last-named additive compounds, the preparation of the following ketones was necessary: *styryl* p-*methoxycinnamylidenemethyl ketone*, yellow crystals, m. p. 115—116°; *styryl* m-*methoxycinnamylidenemethyl ketone*, yellow needles, m. p. 99—101°; p-*methoxystyryl* p-*methoxycinnamylidenemethyl ketone*, yellow needles, m. p. 146—148°; pp'-*dimethoxydicinnamylideneacetone*, greyish-yellow leaflets, m. p. 167—168°, the turbid fusion becoming clear at 177—180°; p-*methoxycinnamylidenemethyl methyl ketone*, yellow leaflets, m. p. 107—108·5°. The general method of synthesis was the condensation of the required aldehyde and ketone in the presence of alkali; thus, styryl *m*-methoxycinnamylidenemethyl ketone was obtained by the interaction of styryl methyl ketone and *m*-methoxycinnamaldehyde (*phenylhydrazone*, m. p. 105—106°).

Fuchsone yielded a *perchlorate*, $CPh_2:C_6H_4:O,HClO_4$, red needles with blue glance, m. p. near 215—216°; a *stannichloride*, $(CPh_2:C_6H_4:O)_2,H_2SnCl_6$, red needles with blue glance, m. p.

210—211°; and a *stannibromide*, $(CPh_2{:}C_6H_4{:}O)_2,H_2SnBr_6$, red prisms with green glance, m. p. 204—205°.

In a similar manner, benzaurin gave a *perchlorate*,

$$OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O,HClO_4,$$

orange-coloured needles with green lustre; a *stannichloride*, $(OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O)_2,H_2SnCl_6$, orange-coloured crystals with green lustre, m. p. 268—269° (decomp.); and a *stannibromide*, $(OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O)_2,H_2SnBr_6$, compact, red crystals with green lustre, m. p. 256—257° (decomp.). Aurin formed a perchlorate, $C(C_6H_4{\cdot}OH)_2{:}C_6H_4{:}O,HClO_4$ (compare Hofmann, Kirmreuther, and Thal, A., 1910, i, 168); a *stannichloride*,

$$[C(C_6H_4{\cdot}OH)_2{:}C_6H_4{:}O]_2,H_2SnCl_6,$$

red crystals with blue glance; and a *stannibromide*,

$$[C(C_6H_4{\cdot}OH)_2{:}C_6H_4{:}O]_2,H_2SnBr_6,$$

red crystals with blue glance.

p-Methoxytriphenylcarbinol gave a *perchlorate*,

$$OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}ClO_4,$$

orange crystals, but no stannichloride was obtainable. D. F. T.

Ozone and its Action on Organic Compounds. CARL DIETRICH HARRIES (*Chem. Zentr.*, 1916, ii, 991—995).—The author has published in book form (1916, pp. 712) an account of his investigations on the action of ozone on organic compounds; the greater part of the results has been previously described, but the following investigations have not heretofore been communicated.

[With KURT OPPENHEIM.]—*Identification of Aliphatic Aldehydes.*—The general reactions for aldehydes have been examined for a series of aliphatic aldehydes. It has been found that the semicarbazones of the lower aldehydes can only be induced to crystallise with great difficulty, whereas the higher aldehydes immediately yield crystalline products. Conversely, the nitrophenylhydrazones of the higher aldehydes are oily, those of the lower members being crystalline. All the aldehydes investigated gave good results with diphenylmethanedimethyldihydrazine (Braun, A., 1908, i, 700). Unsatisfactory results were obtained in attempting to apply Angeli's reaction (action of benzenesulphohydroxamic acid and conversion of the hydroxamic acids formed into their copper salts) to the exact characterisation of aldehydes.

Propaldehyde has D_{19}^{19} 0·8171; n_D^{19} 1·36460; n_α 1·36284; n_γ 1·37315; M_D 15·84; $M_{\gamma-\alpha}$ 0·4. The aldehyde–ammonia compound decomposes at 0°; semicarbazone, oily; *nitrophenylhydrazone*, yellow needles, m. p. 124°. Braun's reagent gives a crystalline *compound*, $C_{21}H_{28}N_4$, m. p. 45°. With pyruvic acid and naphthylamine (Döbner, A., 1894, i, 261, 532) the corresponding *naphthacinchonic acid*, m. p. 278—281°, is formed. The copper salt, prepared in accordance with Angeli's method, gives too high values for copper.

n-Butaldehyde, isolated from the bisulphite compound, has D_{20}^{20} 0·8048; $n_D^{19·5}$ 1·38356; n_α 1·38113; n_γ 1·39137; M_D 20·9; mol. dispersion 0·49. It yields a crystalline *semicarbazone* (after a

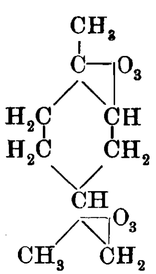
long time), m. p. about 77°. The *nitrophenylhydrazone* forms yellow needles, m. p. 87°. Braun's reagent gives a *compound*, m. p. 70·5°. The *naphthacinchonic acid* from butaldehyde crystallises in needles, m. p. 248°. Angeli's reaction gives a green, copper salt. *iso*Butaldehyde has D_{19}^{19} 0·7917, n_D^{19} 1·37326; n_α 1·37117; n_γ 1·38271; M_D 20·71; mol. dispersion, 0·58. The *semicarbazone* crystallises in prisms, m. p. 121°; the *nitrophenylhydrazone* forms yellow crystals, m. p. 130°. Braun's reagent gives the *compound*, $C_{23}H_{32}N_4$, yellow crystals. With Döbner's reagent the *substance*, $C_{17}H_{15}O_2N$, needles decomposing at about 260°, is formed. Angeli's reaction gives results similar to those obtained with the normal aldehyde. *iso*Valeraldehyde (from the bisulphite compound) has b. p. 92°; D_{20}^{20} 0·7845; n_D^{20} 1·39023; n_α 1·38789; n_γ 1·39940; M_D 25·9; mol. dispersion, 0·7. The *thiosemicarbazone* and *nitrophenylhydrazone*, yellow plates, have m. p.'s 52—53° and 101° respectively. Braun's reagent yields the *substance*, $C_{25}H_{36}N_4$, yellow prisms, m. p. 85°. The *compound*, $C_{18}H_{17}O_2N$, m. p. 250°, is formed by Döbner's reaction. *n*-Heptaldehyde has b. p. 154°, D_{19}^{19} 0·8320; n_D^{19} 1·41370; n_α 1·41105; n_γ 1·42312; M_D 34·59; mol. dispersion, 0·88. The crystalline *semicarbazone* has m. p. 109°; nitrophenylhydrazine and bromophenylhydrazine yield oily precipitates. Reduction of heptaldehyde by sodium amalgam in acetic acid solution yields *n*-heptyl alcohol, b. p. 90°/14 mm. If, however, an excess of sodium is avoided and the solution is not kept acid, diheptylenealdehyde, $CH_3\cdot[CH_2]_5\cdot CH{:}C(CHO)\cdot[CH_2]_4\cdot CH_3$, D^{20} 0·8463, is produced (compare Perkin, T., 1883, **43**, 67). Octaldehyde has b. p. 171—173°; D_{20}^{20} 0·82583; n_D^{20} 1·42167; n_α 1·41957; n_γ 1·43175; M_D 39·3; mol. dispersion, 1·00. The *semicarbazone* has m. p. 98°, whilst the nitrophenylhydrazone and bromophenylhydrazone are oily. Braun's reagent gives the *substance* $C_{31}H_{48}N_4$, yellow plates, m. p. 60°. The *naphthacinchonic acid* of octaldehyde, $C_{21}H_{23}O_2N$, forms yellow leaflets, m. p. 240—243°. The *copper* salt prepared by Angeli's method gives low analytical values for copper. Nonaldehyde has D_{19}^{19} 0·8268; $n_D^{18\cdot 56}$ 1·42417; n_α 1·41876; n_γ 1·43357; M_D 43·8; mol. dispersion, 1·323. It yields an oily precipitate with nitrophenylhydrazine, whilst Braun's reagent gives the *substance*, $C_{33}H_{52}N_4$, yellow leaflets, m. p. 61°. Attempts to separate mixtures of aldehydes by fractional distillation or by conversion into derivatives were unsuccessful.

[With Heinrich Neresheimer.]—*Action of Ozone on certain Terpenes.*—The action of ozone on *d*-limonene in carbon tetrachloride solution leads to the formation of a solid *ozonide*, which when dissolved in ethyl acetate leaves a small residue, probably consisting of oxozonide; the latter passes after some time into the ozonide (formula I). This substance forms a white mass, m. p. 60—65°, $[\alpha]_D^{18}$ $-9{\cdot}32°$, in chloroform solution, which decomposes violently at about 85°. Short treatment with boiling water or dilute acetic acid transforms the ozonide into the *keto-ozonide* (formula II), $C_9H_{14}O_4$, which is a syrup; protracted treatment with boiling water leads to the formation of the diketoaldehyde, $CH_3\cdot CO\cdot[CH_2]_2\cdot CH(CO\cdot CH_3)\cdot CH_2\cdot CHO$, from which the *sub-*

stances (formulæ III and IV) are formed by ring closure, and cannot be separated from one another. Total decomposition of the diozonide by treatment with boiling water during twenty-four hours results in the formation of an oil, b. p. 130—140°/9 mm., from which definite derivatives were not obtained. Oxidation of the ozonide by chromic acid in acetic acid solution at 50—60° leads to the formation of $\beta\delta$-diacetylvaleric acid. In addition to the fairly stable normal ozonides, the ketones yield highly explosive ozonide peroxides. Decomposition with water causes the formation of the acids expected according to theory. 1-Methyl*cyclo*hexene-3-one, when ozonised in chloroform or acetic acid solution, gives a greenish-yellow, very explosive oil, readily soluble in all media except light petroleum. The substance, which is probably the ozonide peroxide, gives the hydrogen peroxide reaction and reduces Fehling's solution after short treatment with boiling water. γ-Acetylbutyric acid (m. p. of hydrate, 38°) is obtained when its aqueous solution is evaporated to dryness in a vacuum.

A mixture of normal *ozonide* and *ozonide peroxide*, a yellow, explosive liquid, is formed by ozonising pulegone in chloroform solution, which is converted by water into β-methyladipic acid. The latter substance, α_D $+2{\cdot}5°$ (in 33% aqueous solution, $l=1$), is also obtained by evaporation of the chloroform solution of the mixture.

A solution of carvone in carbon tetrachloride is converted by ozone into the oily *carvonediozonide*, which, when further ozonised in the same solvent, yields *carvonediozonide peroxide*, unstable, yellow syrup, which explodes after a few hours in a freezing mixture, more rapidly on contact with ice-water and within thirty to thirty-five seconds after mixture with water at 40°. Formaldehyde is formed during the explosion, together with an *oil*, $C_9H_{12}O_5$, which in all probability is the diketo-ozonide (formula V). Total



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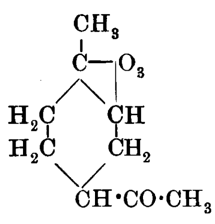

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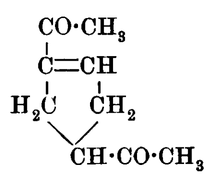

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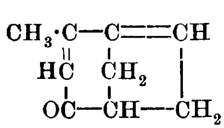

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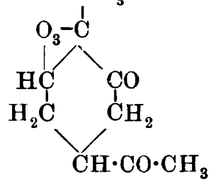

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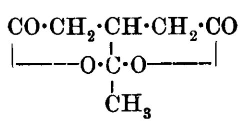


(VI.)

decomposition of the diozonide by steam yields β-acetylglutaric acid (or its ketodilactone, VI), which is also formed from the diketo-ozonide and boiling water.

[With HANS VON SPLAWA-NEYMAN.]—*An Aldehyde from Pinene* (Addendum to A., 1909, i, 247).—Pinonaldehyde, $C_{10}H_{16}O_2$, is a pale yellow oil, b. p. 115—125°, D_4^{19} 1·022, n_D^{19} 1·46867; n_α^{19} 1·46531; M_D 45·75; $[\alpha]_D^{20}$ +14·67°. It is readily volatile with steam, reduces cold silver and Fehling's solutions, and is oxidised by air with formation of pinonic acid. It is readily changed by acids and alkalis or by gentle heating. It reacts with nitrophenylhydrazine. When warmed with benzenesulphohydroxamic acid and acidified, it gives a red coloration with ferric chloride and with copper acetate a green precipitate of the *copper* salt of the corresponding hydroxamic acid. Pinonic acid, obtained by oxidation of the aldehyde with aqueous potassium permanganate, is an oil, b. p. 180—188°/12 mm., $[\alpha]_D^{20}$ +3·9° in chloroform solution. The crystalline *semicarbazone*, $C_{11}H_{19}O_3N_3$, has m. p. 204°. Nopinone, pleasant-smelling oil, $[\alpha]_D^{19}$ +45° (*semicarbazone*, m. p. 167°; *benzylidene* derivative, m. p. 106—107°), is obtained by oxidising the previously described (*loc. cit.*) oil (obtained by fusion of pineneozonide) with permanganate.

[With ROBERT VINER STANFORD.]—*Degradation of Sericin by Ozone* (compare Harries and Langheld, A., 1907, i, 571).—When sericin is ozonised in aqueous solution the products of fission only account for 65% of the original material. The sole uniform product which is formed is a *polypeptide*, which, after purification by repeated solution in water and precipitation with methyl alcohol, has $[\alpha]_D^{18·5}$ −60·1°, C=43·9%, H=5·85%, N=17·5%. Determinations of molecular weight lead to the formula $C_{29}H_{48}O_{16}N_{10}$. It yields a brown *silver* salt, a *lead* compound with lead acetate and ammonia, and a microcrystalline *hydriodide*, containing 14·37% of iodine. Hydrolysis of the polypeptide by acids yielded: CO_2, 8·8%; NH_4Cl, 9·2%; glycine, about 0·5%; alanine, about 1%; valine (or leucine), about 0·3%; serine, 13·1%; aspartic acid, 0·25%; glutamic acid, 0·25%; lysine, 0·35%; and, in addition, arginine. The phenyl group contained in sericine cannot be recognised among the products of ozonisation.

[With EDGAR PAULSEN.]—*Resins.*—A fundamental difference exists between the ozonides of caoutchouc and dammar resin, since the latter is insoluble in carbon tetrachloride and not explosive. Decomposition with water leads to the formation of only a small quantity of acid, the main substance being a solid fission product, insoluble in water. Since other resins behave similarly to dammar resin, it is possible to establish the presence of resins in caoutchouc by ozonisation in carbon tetrachloride solution, and the operation may be made quantitative, since the resin is quantitatively converted into the ozonide. The ozonide obtained by direct solution and ozonisation of dammar resin was not uniform, and the resin was therefore subjected to a preliminary treatment with acetic acid and precipitation with water. All the resins investigated yielded solid ozonides, the m. p.'s of which lay between 53° and 81°.

The solubility of the ozonides was less than that of the resins; they are very sparingly soluble in light petroleum, slightly so in carbon tetrachloride, and yield clear solutions in alcohol, ethyl acetate, acetone, and acetic acid. The fission products are almost insoluble in light petroleum, slightly soluble in carbon tetrachloride, soluble in alcohol, ethyl acetate, acetone, and acetic acid, and, for the most part, in chloroform. A definite phytosterol—or *iso*cholesterol—reaction is not given by the resins, ozonides, or their fission products. The iodine numbers of the ozonides, fission products, and resins are 126—285, 112—238, and 5—152 respectively. The ozonides have C = 47—61%; H = 6—11%; the fission products, C = 60·8—69%; H = 8—10%. The resins may be classified in the following groups: (i) Dammar, mastic, sandarac; (ii) brown and pale dammar copal, recent and fossil kauri copal; (iii) caoutchouc resin and guttapercha resin; (iv) French colophonium, American resin, Mark B, elemi, and galipot. The solubilities of dammar, mastic, and sandarac are very different, those of their ozonides and fission products closely similar. Eighty-two to 83% of dammar resin is soluble in acetic acid; the residue, after solution in light petroleum and precipitation with acetic acid, forms a white, amorphous mass, m. p. 211°, which probably consists of a hydrocarbon, $(C_{10}H_{16})_{16}$. The solubilities of the resins, ozonides, and fission products of the two dammar copals are approximately the same, and this is also true for the kauri copals. M. p.'s of the ozonides, 64° and 68°, 53° and 51° respectively; m. p.'s of resins, 154° and 158°, 92° and 119° respectively. Acid numbers, 198 and 201, 131 and 126 respectively. The solubilities of the resins, ozonides, and fission products of the members of the third group show almost exact agreement. M. p.'s of ozonides, 63° and 70°; m. p.'s of fission products, 92° and 87°. The resins, ozonides, and fission products of group IV also show marked analogies with respect to solubility, etc., for the fuller details of which the original memoir must be consulted. H. W.

Synthesis of Santene. GUST. KOMPPA and S. V. HINTIKKA (*Bull. Soc. chim.*, 1917, [iv], **21**, 13—19. Compare A., 1912, i, 279).—The authors now show that the hydrocarbon obtained from camphenilyl chloride by the action of aniline, diethylaniline, or alcoholic potassium hydroxide (*loc. cit.*), is really a mixture, of which only a small proportion is camphenilene, the main product being santene, b. p. 140—141°, the properties of which agree well with those of natural santene. Further, that *iso*camphenilol is identical with santenol (Semmler's π-norborneol) and *iso*camphenilone with santenone (Semmler's π-norcamphor).

Camphenilol can also be converted into the corresponding hydrocarbon mixture by heating it with anhydrous sodium hydrogen sulphate for one hour at 190—200°. W. G.

Ammonium Soaps of Colophony. LUDWIG PAUL (*Seifenfabrikant*, **36**, 545—546, 567—569; from *Chem. Zentr.*, 1916, ii, 906—907).—An alcoholic solution of colophony solidifies to a stiff jelly when poured into dilute ammonia. Larger quantities are conveniently prepared by grinding γ-pinic acid (KS-acid) with

distilled water and treatment with ammonia in excess. The ammonium soap thus prepared greatly resembles the γ-sodium resin soap. Both form additive compounds with petroleum (compare A., 1915, i, 1066). Aqueous solutions of both resin soaps can be boiled without decomposition; on the other hand, decomposition is always observed with the γ-ammonium soap if this has been prepared with relatively little ammonia. If a concentrated alcoholic solution of colophony is poured into very dilute aqueous ammonia, a solution is obtained which deposits some resinous matter on boiling, and forms a milky emulsion, from which unchanged γ-pinic acid, m. p. 74—76°, is obtained by filtration or by hydrochloric acid. α-Pinic acid, m. p. 101—103°, is formed by addition of hydrochloric acid to the filtrate. Similar precipitates, m. p. about 98°, are obtained when preserved "KS" or colophony powder is treated with ammonia. "KS-acid" does not invariably melt at 76°, but often between 85° and 88°. A resin acid, m. p. 85—87°, is obtained from the calcium salts contained in the filtrate from the precipitation of γ-sodium resin soap by water containing calcium as well as by decomposition of the non-gelatinised ammonium soap. Further, γ-pinic acid, m. p. 85—87°, is obtained from γ-sodium resin soap by means of ether. The higher m. p. is attributed to the entrance of calcium into the resin and its non-removal by hydrochloric acid. A transparent piece of colophony yields the sodium resin soap with sodium hydroxide, from which γ-pinic acid, m. p. 75—76·5°, can be separated. If the latter is washed with much conductivity water the m. p. rises to 85—87°. Further, a substance, m. p. 85—87°, was obtained by the investigation of a two and a-half years old specimen of γ-pinic acid, which, in contrast to the former substance, was soluble in water. γ-Pinic acid gradually becomes transformed into α-pinic acid. Similarly, in the course of time, α-pinic acid is converted into β-pinic acid, m. p. 122—123°. The autoxidation of colophony is to be compared with the conversion of α-pinic acid into the β-compound. This is shown not only by the crumbling of colophony to powder (consisting chiefly of β-pinic acid), but also by the fact that α-pinic acid, m. p. 100—105°, passes within a short period into the β-compound. The α- and β-acids can be separated by the ammonia method, since the ammonium salt of the α-acid is readily decomposed whilst the β-compound shows little or no instability. γ-Pinic acid, the m. p. of which had risen from 74—77° to above 100° during two and a-half years, was stirred with water and ammonia, when a separation of γ-ammonium resin soap was not observed. Before being boiled, the solution deposited considerable quantities (18 grams from 35 grams) of a plastic mass (Kpl), m. p. 95—98°. The filtrate was treated with hydrochloric acid and the precipitate dissolved in conductivity water. Hydrochloric acid precipitated β-pinic acid, m. p. about 120°, from the extracts, so that the substance directly precipitated with ammonia is to be regarded as fairly pure β-pinic acid. Colophony is similarly decomposed with separation of "Kpl." In the "Kpl-substance" a resinous matter intermediate between α- and γ-pinic acids is present (in addition to α-acid), which possibly represents the first product of transformation. Colophony which had been treated

with nitric acid showed the same decomposition when treated with ammonia and boiled; the filtrate also contained β-pinic acid, the latter being characterised by its solubility in water and the formation of fluorescent, resin-lake solutions. Colophony is changed in a few hours by nitric acid in the same manner as by exposure to air for years. This transformation of colophony is attributed to the action of colloidally contained water. On the other hand, colophony can decompose owing to loss of water. Whereas sylvic acid is formed by the action of cold alcohol, hot alcohol causes the formation of γ-abietic acid. Resinous substances may be classified into those soluble in petroleum (γ-pinic acid, sylvic acid, γ-abietic acid) and those insoluble in petroleum (Kpl., α- and β-pinic acids), but the classification is not final. H. W.

Synthesis of Phenol Glucosides. EMIL FISCHER and LUKAS VON MECHEL (*Ber.*, 1916, **49**, 2813—2820).—Many glucosides of the phenols have been obtained in the past by the action of the dry sodium compound on acetobromoglucose in ethereal solution. A new process has now been developed, which consists in warming acetobromoglucose with the phenol in the presence of quinoline, and whereas β-glucosides were always formed in the old way, α-glucosides are produced as well by the new.

Thus, acetobromoglucose (50 grams), phenol (160 grams), and quinoline (19 grams) are heated on the water-bath for an hour or so, the base is extracted with dilute sulphuric acid and ether, and the excess of phenol is removed by heating at 100°/0·2 mm. The residue is a mixture of α- and β-glucosides, which are separated by crystallisation from carbon tetrachloride. Tetra-acetyl-β-phenolglucoside is sparingly soluble in the cold, and is deposited in an almost pure condition, $[\alpha]_D^{20}$ $-28·94°$; it may be hydrolysed by barium hydroxide solution to β-phenol-*d*-glucoside, $2H_2O$, m. p. 175—176° (corr.), $[\alpha]_D^{20}$ $-71·9°$, in the usual way (compare Fischer and Armstrong, A., 1901, i, 671).

Tetra-acetyl-α-phenolglucoside is present in the same amount in the mother liquor; it has m. p. 115° (corr.), $[\alpha]_D^{20}$ $+164·9°$ (benzene), and the corresponding *α-phenol-*d*-glucoside* crystallises with $1H_2O$ in slender needles, m. p. 173—174° (corr.), $[\alpha]_D^{20}$ $+180°$.

The rate of hydrolysis of these glucosides was compared with that of α-methylglucoside under the same conditions, and it was found that during the time that 4·5% of the latter is hydrolysed, 32% of the β-phenolglucoside and 68% of the α-phenolglucoside are hydrolysed. The remarkable feature of this result is not that the phenolglucosides are so easily hydrolysed, but that the β-form is more quickly changed than the α-isomeride, which is the reverse of what obtains with the methylglucosides.

The β-phenolglucoside is hydrolysed by emulsin, but not by yeast extract; the α-glucoside behaves in the opposite way.

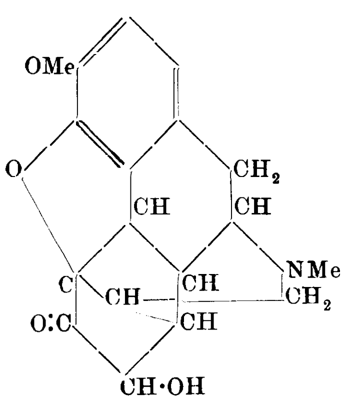
J. C. W.

The Cinchona Alkaloids. XVII. Degradation of Cincholeupone to 4-Aminomethyl-3-ethylpiperidine. PAUL RABE [with RICHARD PASTERNACK] (*Ber.*, 1916, **49**, 2753—2756).—In

his last papers (1913) the author had foreshadowed further developments in the chemistry of the scission products of the cinchona alkaloids, including the partial synthesis of the bases by combining cincholeupone with various cinchonic or quinic acids, and he complains of Kaufmann's competition in this field (see this vol., i, 50). He now describes the conversion of cincholeupone (3-ethylpiperidine-4-acetic acid) through the ester into the *hydrazide*, colourless needles, m. p. 115°, then into the azide, and finally through the urethane or carbamide, into 4-*aminomethyl*-3-*ethylpiperidine*, which is a colourless base, b. p. 110°/12 mm., and forms a *diplatinichloride*, B,H_2PtCl_6,H_2O, orange needles, decomp. 255°, and a *di-aurichloride*, $B,2HAuCl_4,H_2O$, golden leaflets, decomp. 205°. J. C. W.

Thebaine. VI. Transformation of Thebaine into Hydroxycodeinone and its Derivatives. MARTIN FREUND and EDMUND SPEYER (*J. pr. Chem.*, 1916, [ii], **94**, 135—178).—The connexion between thebaine and codeine has been demonstrated in various ways by Knorr and his colleagues on the one hand and in Freund's laboratory on the other (see A., 1903, i, 849; 1906, i, 303, 449). It has now been found that when thebaine, dissolved in boiling acetic acid, is treated with 30% hydrogen peroxide, or is oxidised by potassium dichromate and sulphuric acid, it is converted into a hydroxylic ketone which contains one oxygen atom more and a methylene group less than the original substance. It is not the amine-oxide formed under slightly different conditions (A., 1911, i, 76), because it is indifferent to the action of sulphurous acid, but a hydroxycodeinone, for it yields the same oxime as bromocodeinone (A., 1906, i, 303). Many derivatives of this compound are described, and the constitution of them is discussed at some length on the basis of Knorr's formula and the more preferable one recently proposed, which contains no aliphatic ethylene linkings (A., 1916, i, 738).

Hydroxycodeinone, probably of the annexed formula, crystallises in tablets, decomp. 275°, and forms a *hydrochloride*, columns, decomp. 285—286°, and the above-mentioned oxime, decomp. 279—280°. The *methiodide*, small prisms, decomp. 247°, can be demethylated in the usual way, and the *methiodide* of the secondary base so formed, leaflets, decomp. 267°, also loses trimethylamine readily enough, without, however, yielding a crystallisable nitrogen-free compound.



The *acetate* crystallises in elongated tablets, m. p. 185—186°, forms a *hydrochloride*, decomp. 258°, and an *oxime*, $1H_2O$, small

prisms, m. p. 148°, and reacts with cyanogen bromide to form *cyanonorhydroxycodeinone*, [N·CN instead of NMe in the above formula], which is a weak base and separates in well-developed tablets, m. p. 255°. The *benzoate* crystallises in columns, m. p. 245—247°.

When hydroxycodeinone is boiled with 30% hydrogen peroxide it is oxidised to the amine–oxide [NMe:O], which forms a *picrate*, in small, rhombic crystals, decomp. 187—188°. Other attempts to degrade the compound by oxidation were fruitless, but three different products have been obtained by reduction. With zinc dust and formic acid the ketone group is attacked, and *hydroxycodeine* results, in prismatic rods, m. p. 293°. This is insoluble in sodium hydroxide, and forms a *hydrobromide*, decomp. 290°, and a *monoacetate*, leaflets, decomp. 283°. Stannous chloride apparently opens the oxide ring, with the formation of the yellow, phenolic *hydroxythebainone*, which yields a *hydrochloride*, stout columns, decomp. above 280°, and an *oxime*, decomp. 255°. On the other hand, the ketone–alcohol nature of the base is preserved when catalysed hydrogen or sodium hyposulphite is used as the reducing agent. In this case, one of the links in the "bridge" (across the ring at the bottom of the formula) disappears. The *hydroxydihydrocodeinone* so formed crystallises in elongated, jagged columns, m. p. 218—220°, and yields a *hydrochloride*, m. p. 268—270°, $[\alpha]_D$ −125·2°, in water; a *hydriodide*, m. p. 189—190°; the *hydrochloride* of an *oxime*, decomp. 275—278°; a *phenylhydrazone*, tablets, m. p. 204°; an *acetate*, leaflets, m. p. 215—216° (*hydrochloride*, decomp. 275°; *oxime hydrochloride*, needles, m. p. 230—231°; free *oxime*, tablets, m. p. 179—180°); and a *benzoate*, m. p. 275—276°. A *tautomeride*, highly refractive scales, m. p. 219—220°, is formed if hydroxydihydrocodeinone is warmed with sodium amalgam and alcohol.

Although no product free from nitrogen could be obtained from hydroxycodeinone (see above), such can be realised in the case of hydroxydihydrocodeinone. The *methiodide*, stout prisms, decomp. 251°, yields a secondary *base*, stellar aggregates, m. p. 115° (*oxime*, lanceolate leaflets, m. p. 185—186°), the *methiodide* of which, leaflets, m. p. 255—256°, readily parts with trimethylamine to form "*hydroxydihydrocodeone*," $C_{17}H_{16}O_4$. This crystallises in rods, m. p. 214—215°, and forms an *oxime*, large spikes, m. p. 211°.

If hydroxydihydrocodeinone is reduced with sodium amalgam, or amalgamated zinc and hydrochloric acid, or by electrolysis at a lead cathode, then the oxide ring is ruptured and the corresponding *hydroxydihydrothebainone* is produced. This forms nodular groups, m. p. 145°, and yields a *hydrochloride*, decomp. 310°, $[\alpha]_D$ −52·47°, a *perchlorate*, decomp. 270°, an *oxime*, stout prisms, m. p. 222°, a *monoacetate*, m. p. 214°, insoluble in sodium hydroxide, and the *perchlorate* of a *methyl ether*,

$$C_{19}H_{25}O_4N,HClO_4,H_2O,$$

long columns, m. p. 134°.

Hydroxydihydrothebainone can also be indirectly degraded to a compound free from nitrogen. The *methiodide*, $1H_2O$, needles,

decomp. 210°, yields a secondary *base*, m. p. 242—243°, $[\alpha]_D$ $-81.88°$ (in dilute acetic acid) (*hydriodide*, quadratic tablets, m. p. 158°), but the methiodide of this is a resinous substance which, although it loses trimethylamine readily, does not give a definite product. If the secondary base is reduced with hydrogen and colloidal palladium, however, the resulting *demethylated hydroxytetrahydrothebainone*, $C_{19}H_{27}O_4N$, m. p. 239—240°, $[\alpha]_D$ $-45.25°$ (in dilute acetic acid) yields a *methiodide*, which loses trimethylamine readily and forms "7-*hydroxytetrahydrothebaone*," $C_{17}H_{20}O_4$, in groups of feathery needles, m. p. 143—144°.

If the treatment suitable to the oxidation of thebaine to thebaine oxide is prolonged (*ibid.*), a small quantity of *dehydrothebaine*, $C_{19}H_{19}O_3N$, is formed as well, in yellow prisms, m. p. 178—180°. The two methoxyl groups are intact in this, and the base forms a *methiodide*, tablets, decomp. 177°. J. C. W.

New Cases of Isomerism. GUSTAV HELLER (*Ber.*, 1916, **49**, 2757—2774).—Lactams are usually regarded as substances which contain such a labile hydrogen atom that as a rule they only exist in one of the desmotropic forms. This is not always so, however, for the author has shown that the two isomerides represented by the formulæ

$$C_6H_4\Big<\begin{array}{l}CO-CH\\ NH\cdot CMe\end{array} \quad \text{and} \quad C_6H_4\Big<\begin{array}{l}C(OH){:}CH\\ N{=\!=\!=}CMe\end{array},$$

are distinct individuals (A., 1908, i, 913). A case of desmotropism seems to be exhibited, on the other hand, by 3-*hydroxy*-2-*phenylindazole*. A stable form of this is obtained by heating hydrazobenzene-*o*-carboxylic acid with acetic anhydride. It crystallises in colourless needles or rods, m. p. 204°, and forms a *benzoate*, long spikes, m. p. 180.5°, but it changes into the labile ketonic modification, m. p. 217°, by solution in phosphoryl chloride. This is transformed into the hydroxylic form by successive crystallisations, and it is the modification which Freundler has described (A., 1907, i, 158). The change is represented thus:

$$C_6H_4\Big<\begin{array}{c}CO\\ NH\end{array}\Big>NPh \longrightarrow C_6H_4\Big<\begin{array}{l}C(OH)\\ N\text{———}\end{array}\Big>NPh.$$

A particularly interesting case of the wandering of a hydrogen atom is furnished by isatin. The lactam and lactim forms of this have long been known in the methyl compounds *A* and *B*. The remaining alternative, *C*, which is designated "isatol," has now been isolated:

$$\underset{A.}{C_6H_4\Big<\begin{array}{c}CO\\ NMe\end{array}\Big>CO} \quad \underset{B.}{C_6H_4\Big<\begin{array}{c}CO\\ N\end{array}\Big>C\cdot OMe} \quad \underset{C.}{C_6H_4\Big<\begin{array}{l}C(OH)\\ N\text{———}\end{array}\Big>CO.}$$

This is obtained as follows: Isatin, dissolved in hot alcohol, is shaken with silver acetate solution, when the N-*silver* salt separates at once as a greyish-red powder, which gives a deep bluish-red solution in pyridine. This silver salt is warmed with benzoyl chloride

and benzene, the silver chloride is removed, and the filtrate left to crystallise. Isatol separates, and is purified ultimately by crystallisation from methylal. *Isatol* forms red prisms, m. p. 194·5°, is insoluble in sodium carbonate or ammonia, but soluble with orange-red colour in sodium hydroxide. This solution becomes pale on heating, and then acids precipitate ordinary isatin. Acetic anhydride, benzoyl chloride, phenylhydrazine, sodium hydrogen sulphite, methyl iodide, and sodium nitrite have no action, but diazomethane gives the corresponding *methyl ether*, as a pale yellow, amorphous substance.

The function of the hydrogen atom in each of the three positions is therefore revealed. It has the most acidic properties in the imino-combination. The evidence in support of this is the fact that isatin dissolves in ammonia whereas isatol does not; isatin decomposes silver acetate, and the ethyl ether of the α-oxime (Baeyer, 1882) gives deep blue solutions in sodium hydroxide, whereas the ethyl ether of the β-oxime is only phenolic and gives a yellow solution. α-Isatoxime, $C_6H_4<\substack{CO\\NH}>C:N\cdot OH$, is conveniently obtained by the action of hydroxylamine on *O*-methylisatin (A., 1907, i, 442). It changes into benzoylenecarbamide, $C_6H_4<\substack{CO-NH\\NH\cdot CO}$, on warming with sodium hydroxide.

The various salts of isatin and its ethers and oximes (see also *ibid.*) owe their differences of colour mainly to the different attachments of the metal, the N-salts being usually deeper in colour than the O-salts. The question whether the metallic atom is linked to nitrogen or oxygen or even to carbon should, therefore, be taken into account in other cases of salt formation, and several examples are discussed at length. J. C. W.

Oxindole. GUSTAV HELLER [with HERMANN HEINE] (*Ber.*, 1916, **49**, 2775—2778).—It has already been shown that dioxindole forms a violet salt which quickly changes into a colourless isomeride (A., 1904, i, 416). The change is most probably that of an N-salt into an O-salt, thus:

$$C_6H_4<\substack{CH(OH)\\NNa}>CO \longrightarrow C_6H_4<\substack{CH(OH)\\N}\geqslant C\cdot ONa.$$

It has now been tested whether oxindole undergoes similar reactions, but the results obtained are obscure and inconclusive.

Oxindole is best obtained by reducing *o*-nitrophenylacetic acid with ammonia and ferrous sulphate. If sodium hydroxide and ferrous sulphate are used, the product is *o*-azoxyphenylacetic acid (Reissert, A., 1909, i, 51). Oxindole reacts with sodium ethoxide to form a colourless *salt*, probably of the formula

$$C_6H_4<\substack{CH_2\\N}\geqslant C\cdot ONa,H_2O.$$

This reacts with benzoyl chloride to form the normal benzoate,

m. p. 192°, and also a *tribenzoyl* derivative, $C_6H_4<\genfrac{}{}{0pt}{}{CBz_2}{NBz}>CO$, tufts of pale yellow needles, m. p. 172—173°. J. C. W.

The so-called Chromoisomerism of Salts of Phenylmethylacridinium. F. KEHRMANN and KNUT STAHRFOSS (*Ber.*, 1917, **50**, 24—30).—Just as the pure salts of 9-phenylacridine have all the same colour (A., 1916, i, 744), so the salts of phenylmethylacridine are all yellow, except the iodide, which is normally darker than the other haloids, and the sulphite, which exhibits various colours. Hantzsch has recently reinvestigated the sulphites (A., 1916, i, 836), but it is now claimed that his actual analytical data support Kehrmann's views very fully, whilst the "theoretical" data were wrongly calculated. It is maintained that the supposed brown anhydride is a monohydrate, which necessitates a revision of the formulæ assigned to the various "solvates."

The authors recognise a yellow, very unstable, normal sulphite, $\left(CPh<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>NMe\right)_2SO_3$; a quinhydrone-like salt compounded of phenylmethylacridine and phenylmethylacridinesulphonic acid,

$$NMe<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CPh\cdot SO_2\cdot O\cdot NMe<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CPh,$$

which is reddish-brown to olive-green, according to the amount and nature of the combined solvent; and the colourless alkali salts of this acid. J. C. W.

Compounds of Pyridine with the Alkali Metals. III. BRUNO EMMERT (*Ber.*, 1917, **50**, 31—35. Compare A., 1916, i, 668).—When the sodium compound of pyridine, C_5H_5NNa, is treated with moist ether, a very readily oxidisable mixture of tetrahydrodipyridyls is formed. The constitution of this is revealed by the nature of the products of auto-oxidation, one of them being 4 : 4′-dipyridyl, m. p. 111—112°, b. p. 302° (corr.), and the other a yellow, hydroxylic *compound*, $C_{10}H_{12}ON_2$ (or perhaps a hydrate of this), which yields 2 : 2′-dipyridyl, m. p. 69·5°, when heated with sulphuric acid at 280°. J. C. W.

Action of Hydroxylamine and Hydrazine on Benzoylphenylethylene Oxide. OSKAR WIDMAN (*Ber.*, 1916, **49**, 2778—2782. Compare A., 1916, i, 406).—The work of two of the author's colleagues on substituted benzoylphenylethylene oxides (following abstracts) has thrown more light on compounds of this class, and the earlier views with regard to the "oximes" and "hydrazone" are now modified.

The "γ-oxime" is apparently the true oxime, probably mixed with a stereoisomeride, the "δ-oxime." It changes very readily into the so-called "α-oxime," m. p. 169—169·5°, which is really 4-*hydroxy*-3 : 5-*diphenyl*-4 : 5-*dihydro*iso*oxazole*, thus:

$$\underbrace{OH\cdot N{:}CPh\cdot CH—CHPh}_{O} \longrightarrow N<\genfrac{}{}{0pt}{}{CPh\cdot CH\cdot OH}{O—CHPh}$$

This forms an *acetate*, in leaflets, m. p. 175—176°, when boiled with acetic anhydride and a drop of sulphuric acid for a few moments. A characteristic reaction of these ethylene oxides is that they liberate iodine when boiled with glacial acetic acid and potassium iodide. The "γ-oxime" does this, but not the "α-oxime."

The so-called "β-oxime," m. p. 161°, is perhaps a stereoisomeride of the *iso*oxazole, "α." A further isomeride can be obtained by boiling the chlorohydrin of benzoylphenylethylene oxide with excess of alcoholic hydroxylamine hydrochloride. The chlorohydrin is now recognised to be *β-chloro-β-benzoyl-α-phenylethyl alcohol*, CHClBz·CHPh·OH, and the new hydroxylamine derivative is therefore *5-hydroxy-3:5-diphenyl-4:5-dihydro*iso*oxazole*,

$$N\!\!<\!\!\begin{array}{l}CPh\cdot CH_2\\ |\qquad\ \ |\\ O\!\!-\!\!\!-\!\!CPh\cdot OH\end{array};$$

it crystallises in leaflets, m. p. 173°, and changes into diphenyl*iso*-oxazole on heating with acetic anhydride and a drop of sulphuric acid.

The so-called "hydrazone," m. p. 209°, is really *4-hydroxy-3:5-diphenylpyrazoline*, $N\!\!<\!\!\begin{array}{l}CPh\cdot CH\cdot OH\\ NH-CHPh\end{array}$, for it yields a *nitroso*-compound, in yellow pyramids or needles, m. p. 155° (decomp.).

J. C. W.

Anisoylphenylethylene Oxide. HENRIK JÖRLANDER (*Ber.*, 1916, **49**, 2782—2795).—ω-Chloro-*p*-methoxyacetophenone condenses with benzaldehyde in the presence of sodium ethoxide, like the simple ω-chloroacetophenone (A., 1913, i, 1220), to form *anisoylphenylethylene oxide*, $OMe\cdot C_6H_4\cdot CO\cdot CH\!\!<\!\!\begin{array}{l}CHPh\\ O\end{array}$, in rhombic tablets, m. p. 82°. This can be converted into the corresponding yellow diketone, anisylbenzylglyoxal,

$$OMe\cdot C_6H_4\cdot CO\cdot CO\cdot CH_2Ph,$$

which will be described in a forthcoming paper. It forms two chlorohydrins. When covered with cold alcoholic hydrogen chloride, it yields *β-chloro-β-anisoyl-α-phenylethyl alcohol*,

$$OMe\cdot C_6H_4\cdot CO\cdot CHCl\cdot CHPh\cdot OH,$$

in colourless prisms, m. p. 117°, the above diketone being formed at the same time. This chlorohydrin is reconverted into the oxide when treated with cold sodium ethoxide solution, and it forms an *acetate* which crystallises in leaflets, m. p. 72°. When the oxide is treated with acetyl chloride in moist acetic acid, or with hydrogen chloride in benzene solution, *β-chloro-α-anisoyl-β-phenylethyl alcohol* is formed, in small needles, m. p. 110°. This yields the above diketone when treated with sodium ethoxide solution, forms an acetate, m. p. 84°, and may be oxidised to a diketone, which condenses with *o*-phenylenediamine to give *2-α-chlorobenzyl-3-anisylquinoxaline*, $\begin{array}{l}OMe\cdot C_6H_4\cdot C{:}N\\ CHPhCl\cdot C{:}N\end{array}\!\!>\!\!C_6H_4$, m. p. 92—93°.

Anisoylphenylethylene oxide gives an *oxime*, leaflets, m. p. 125—126°, when left with hydroxylamine hydrochloride and sodium acetate (2 mols. each); this changes into 4-*hydroxy*-5-*phenyl*-3-*anisyl*-4 : 5-*dihydro*iso*oxazole*, slender needles, m. p. 150°, in alkaline solutions or on warming with alcohol and a drop of hydrochloric or sulphuric acid, thus:

$$\begin{array}{l} OMe\cdot C_6H_4\cdot C\cdot CH{-}CHPh \\ \quad OH\cdot N \diagdown O \diagup \end{array} \longrightarrow O{<}\begin{array}{l} N{=\!=}C\cdot C_6H_4\cdot OMe \\ CHPh\cdot CH\cdot OH \end{array}$$

This compound is also obtained by leaving an alcoholic solution of the oxide with hydroxylamine hydrochloride (2 mols.) or by boiling the chlorohydrin, m. p. 110°, with hydroxylamine hydrochloride; its *acetate* has m. p. 128°. The isomeric 5-*hydroxy*-5-*phenyl*-3-*anisyl*-4 : 5-*dihydro*iso*oxazole*, glistening leaflets, m. p. 185°, is obtained in the same way from the other chlorohydrin, m. p. 117°, or by boiling an alcoholic solution of the oxide with hydroxylamine hydrochloride (3 mols.); its *acetate* has m. p. 152—153°. If, in the last reactions, the action of hydroxylamine is prolonged, 4-*oximino*-5-*phenyl*-3-*anisyl*-4 : 5-*dihydro*iso*oxazole*, $O{<}\begin{array}{l} N{=\!=}C\cdot C_6H_4\cdot OMe \\ CHPh\cdot C{:}N\cdot OH \end{array}$, is also formed, in colourless, microscopic needles, m. p. 225° (decomp.).

When boiled with alcoholic hydrazine hydrate, anisoylphenylethylene oxide forms 4-*hydroxy*-5-*phenyl*-3-*anisylpyrazoline*, $NH{<}\begin{array}{l} N{=\!=}C\cdot C_6H_4\cdot OMe \\ CHPh\cdot CH\cdot OH \end{array}$, in colourless needles, m. p. 176—177° (decomp.), the *diacetyl* derivative of which has m. p. 195—196°. The base forms a *nitroso*-compound, yellow needles, m. p. 148° (decomp.), which yields an *acetate*, pale yellow prisms, m. p. 177° (decomp.), and gives rise to 5-*phenyl*-3-*anisylpyrazole* on boiling with glacial acetic acid or alcoholic alkali hydroxide. This crystallises in needles, m. p. 159—160°, and forms an *acetyl* derivative, m. p. 88°.

Anisoylphenylethylene oxide also reacts with phenylhydrazine in boiling acetic acid, yielding 1 : 5-*diphenyl*-3-*anisylpyrazole*, in long needles, m. p. 140°, which readily forms a bromine *compound*, $C_{22}H_{17}ON_2Br$, m. p. 149°. With an excess of phenylhydrazine in cold acetic acid, however, the product is *α-hydroxy-β*-N$^{\alpha}$-*phenylhydrazinoethyl anisyl ketone phenylhydrazone*,

$$OMe\cdot C_6H_4\cdot C({:}N\cdot NHPh)\cdot CH(OH)\cdot CHPh\cdot NPh\cdot NH_2,$$

which crystallises in needles, m. p. 166° (decomp.), and readily suffers condensation to 3-anisyl-1 : 5-diphenylpyrazole. It forms a *nitroso*-compound,

$$OMe\cdot C_6H_4\cdot C({:}N\cdot NHPh)\cdot CH(OH)\cdot CHPh\cdot NPh\cdot NO,$$

in pale yellow leaflets, m. p. 156—157° (decomp.), and a *benzylidene* compound, m. p. 141°, and reacts with bromine to give a *compound*, $C_{22}H_{18}ON_2Br_2$, m. p. 165—166°. J. C. W.

Aromatic Oxido-compounds. [Ethylene Oxides]. Sven Bodforss (*Ber.*, 1916, **49**, 2795—2813. Compare preceding abstracts).—The condensation of aldehydes with ω-bromoaceto-

phenone is not a general reaction, but the presence of a halogen atom or nitro-group in the nucleus is distinctly favourable to the production of substituted ethylene oxides. *m*-Nitrobenzaldehyde reacts particularly well, and many properties of the benzoyl-*m*-nitrophenylethylene oxide so formed are now described.

Benzoyl-m-*nitrophenylethylene oxide*, $NO_2\cdot C_6H_4\cdot CH<\begin{matrix}CHBz\\ | \\ O\end{matrix}$, crystallises from alcoholic solutions when these are slowly cooled in shimmering, prismatic leaflets, or when quickly cooled in long, matted needles, m. p. 118°. *Benzoyl*-p-*nitrophenylethylene oxide* forms leaflets, m. p. 148°. *Benzoyl*-p-*chlorophenylethylene oxide* crystallises in large, thin tablets, m. p. 79—80°. *Benzoyl*-p-iso*propylphenylethylene oxide* has m. p. 76°, and slowly suffers oxidation to benzoylformic acid and cumenaldehyde.

These ethylene oxides can be made to condense again with ω-bromoacetophenone to form butadiene dioxides. Thus, in the last preparation, some *α-benzoyl-β-phenyl-δ*-p-iso*propylphenylbutadiene dioxide*, $\begin{array}{c}CHBz\cdot CPh\cdot CH{-}CH\cdot C_6H_4Pr^{\beta}\\ \diagdown\diagup \qquad\quad \diagdown\diagup \\ O \qquad\qquad O\end{array}$, silky needles, m. p. 129°, is formed, as well as the simple oxide. *α-Benzoyl-β-phenyl-δ*-p-*nitrophenylbutadiene dioxide* crystallises in shimmering leaflets, m. p. 207° (corr.), and *α-benzoyl-β-phenyl-δ*-p-*chlorophenylbutadiene dioxide* has m. p. 171°.

The oxides readily lose oxygen and change into ethylenes when warmed with glacial acetic acid and potassium iodide. Thus, benzoyl-*m*-nitrophenylethylene oxide yields phenyl *m*-nitrostyryl ketone, and the corresponding butadiene dioxide gives *α-benzoyl-β-phenyl-δ*-p-*nitrophenyl-$\Delta^{\alpha\gamma}$-butadiene*,

$$CHBz{:}CPh\cdot CH{:}CH\cdot C_6H_4\cdot NO_2.$$

This exists in a sparingly soluble form, pale yellow crystals, m. p. 251° (corr.), and in a very soluble modification, m. p. 215° (corr.), which is rose-red if prepared in the dark, but becomes lemon-yellow in the light, and changes into the less fusible isomeride when boiled with glacial acetic acid. *α-Benzoyl-β-phenyl-δ*-p-*chlorophenyl-$\Delta^{\alpha\gamma}$-butadiene* also exists in a more stable, sparingly soluble form, m. p. 263° (corr.), and in a labile form, m. p. 190° (corr.).

An isomeride of benzoyl-*m*-nitrophenylethylene oxide, namely, *phenyl* m-*nitro-α-hydroxystyryl ketone*,

$$COPh\cdot CH{:}C(OH)\cdot C_6H_4\cdot NO_2,$$

can be obtained by the gradual addition of potassium hydroxide to a boiling methyl-alcoholic solution of αβ-dibromo-β-*m*-nitrophenylpropiophenone, the product of the action of bromine on *m*-nitrophenyl styryl ketone. The compound crystallises in pale yellow, coral-like aggregates, m. p. 135°, titrates as a pure enol, forms a *copper* salt, and yields *m*-nitrobenzoic acid and benzoylformic acid on oxidation. The *methyl ether*,

$$CHBz{:}C(OMe)\cdot C_6H_4\cdot NO_2,$$

matted filaments, m. p. 91°, and the *α-bromo*-compound,

$$CHBz{:}CBr\cdot C_6H_4\cdot NO_2,$$

long needles, m. p. 97—98°, are also formed in this reaction, and by suitably arranging the conditions they can be made the chief products.

Benzoyl-*m*-nitrophenylethylene oxide and its enolic isomeride react with hydrazine hydrate to form 3-*phenyl*-5-m-*nitrophenylpyrazole*, $N\negthinspace<\negthinspace\begin{array}{l}CPh\cdot CH\\ NH-C\cdot C_6H_4\cdot NO_2\end{array}$, m. p. 205°, which is feebly basic and yields an *acetyl* derivative, m. p. 156°. Similarly, phenylhydrazine gives rise to 1:3-*diphenyl*-5-m-*nitrophenylpyrazole*, yellow, hexagonal prisms, m. p. 131—132°, which may also be prepared by the action of boiling alcoholic silver nitrate solution on the corresponding *pyrazoline*, $N\negthinspace<\negthinspace\begin{array}{l}CPh-CH_2\\ NPh\cdot CH\cdot C_6H_4\cdot NO_2\end{array}$, a dark red compound, m. p. 149°, which is obtained by boiling phenyl *m*-nitrostyryl ketone with phenylhydrazine and acetic acid (compare Auwers and Voss, A., 1910, i, 70).

The chlorohydrin of the ethylene oxide, *β-chloro-α-benzoyl-β*-m-*nitrophenylethyl alcohol*, $OH\cdot CHBz\cdot CHCl\cdot C_6H_4\cdot NO_2$, m. p. 100—100·5°, is obtained by the action of dry hydrogen chloride on a suspension of the oxide in carbon tetrachloride and chloroform. It forms unstable *additive* compounds with solvents; for example, with 3EtOH, with $1MeCO_2H$, and $1CCl_4$. The *benzoate* has m. p. 147°. With phenylhydrazine it forms a true *phenylhydrazone*, pale yellow cubes, m. p. 104°, which changes into 4-*hydroxy*-1:3-*diphenyl*-5-m-*nitrophenylpyrazoline*, long, orange needles, m. p. 200°, if the action is prolonged, thus:

$$NHPh\cdot N{:}CPh\cdot CH(OH)\cdot CHCl\cdot C_6H_4\cdot NO_2 \longrightarrow N\negthinspace<\negthinspace\begin{array}{l}CPh-CH\cdot OH\\ NPh\cdot CH\cdot C_6H_4\cdot NO_2\end{array}$$

This reacts with benzoyl chloride in cold pyridine to form the O-*benzoate*, m. p. 156—157°, but when warmed with the agent it loses water and changes to the above pyrazole, m. p. 131—132°.

The chlorohydrin is reconverted into the oxide when treated with alcoholic alkali hydroxide, but it loses hydrogen chloride in the other possible way when heated at 80° under reduced pressure, forming *phenyl* m-*nitro-α-hydroxystyryl ketone*,

$$OH\cdot CBz{:}CH\cdot C_6H_4\cdot NO_2,$$

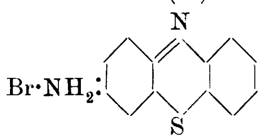
in pale yellow prisms, m. p. 118°. This behaves as an *αβ*-diketone, forming with *o*-phenylenediamine 2-*phenyl*-2-m-*nitrobenzylquinoxaline*, long, felted needles, m. p. 121—122°, and suffering the benzil transformation to *phenyl*-m-*nitrobenzylglycollic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CPh(OH)\cdot CO_2H$, long needles, m. p. 166—167°.

J. C. W.

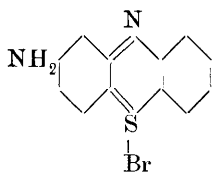
Vat Dyes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat., 1209163; from *J. Soc. Chem. Ind.*, 1917, **36**, 211).—Vat dyes are obtained by heating para-quinones with arylaminoacetic acids in a suitable solvent. The *substance*, $NMePh\cdot C_6H_2O_2\cdot NMePh$, brown, crystalline powder, m. p. 232° (decomp.), is specially claimed. It yields a colourless vat with alkaline hyposulphite, from which it gives yellow tints on animal fibres. H. W.

Dyes of the Methylene-blue Group. III. Moderated Action of Aliphatic Amines on Phenazthionium Salts. F. KEHRMANN [with ADRIEN ROBERT and MAURICE SANDOZ] (*Ber.*, 1916, **49**, 2831—2838. Compare A., 1916, i, 435, 673).—In the earlier papers it was shown that amines can react with phenazthionium salts, especially the perbromide, to give dyes of the methylene-blue series. Under some conditions the reaction can be so modified that only one amino-group is introduced.

Thus, if phenazthionium perbromide is triturated with alcoholic ammonia an orange solution of a thiazime is obtained. If this is allowed to evaporate and the residue is dissolved in water and mixed with sodium bromide, thiazime bromide (I) is deposited, but if the solution is acidified first and then treated in the same way, a more greenish-blue product is obtained, which apparently contains the isomeride (II):

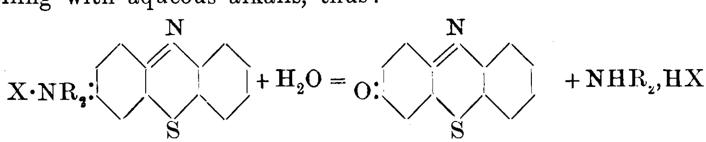


(I.)



(II.)

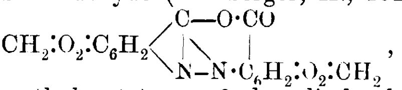
Similarly, if an alcoholic solution of dimethylamine is added to a suspension of the perbromide in ether and alcohol until a bluish-violet solution is obtained, and the further action of the base is stopped by neutralisation, the following substances are produced: bromophenazthione, which is soluble in ether; *dimethylthiazime*, which can be precipitated as the *perchlorate* in very long, bronzy needles, or as the violet *platinichloride*; reddish-violet methylthiazime (?), which can be extracted by ether from an alkaline solution (sodium carbonate) and forms a dark violet-brown perchlorate; and methylene-blue. Diethylamine behaves in the same way; *diethylthiazime perchlorate* forms long, metallic-looking, violet needles, and the *platinichloride* almost black granules with bronzy lustre. These alkylated thiazimes yield phenazthione on boiling with aqueous alkalis, thus:



The absorption spectra of solutions of the para-quinonoid mono-acid salts of six thiazimes were determined. The chief characteristic is the appearance of a band in the ultra-violet with a maximum at about $\lambda = 290\ \mu\mu$. This seems to be a feature common to all tri-cyclic phenazthionium dyes (compare *ibid.*, 673). J. C. W.

Azoxycatechol Ethers and Related Substances. GERTRUDE MAUD ROBINSON (T., 1917, **111**, 109—121).—4:5:4′:5′-Dimethylenetetraoxyazobenzene-2:2′-dicarboxylic acid is obtainable

from 6-nitro-3 : 4-methylenedioxybenzoic acid, not only by heating with nitrobenzene (Robinson and Robinson, T., 1914, **105**, 1466; A., 1916, i, 166), but also by treating with hot aqueous sodium or potassium hydroxide, in which case it is accompanied by *azoxypiperonal*, $CH_2{:}O_2{:}C_6H_2(CHO){\cdot}NO{:}N{\cdot}C_6H_2(CHO){:}O_2{:}CH_2$. This substance can also be produced by the action of sodium methoxide on nitropiperonal in methyl-alcoholic solution; it is changed by nitric acid into a *nitrodimethylenetetraoxyazoxybenzenecarboxylic acid*, $CO_2H{\cdot}C_6H_2({:}O_2{:}CH_2){\cdot}NO{:}N{\cdot}C_6H_2({:}O_2{:}CH_2){\cdot}NO_2$, which is attacked by sodium hydroxide solution with formation of a colourless, crystalline substance giving a reddish-violet solution in aqueous sodium hydroxide, and of *2-nitro-4 : 5 : 4′ : 5′-dimethylenetetraoxyazobenzene-2′-carboxylic acid.* When heated alone, or with acetic acid or nitrobenzene, azoxypiperonal behaves similarly to azoxybenzaldehyde (Bamberger, A., 1911, i, 694), yielding the *lactone*,



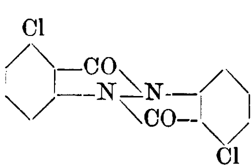
, of 3-hydroxy-5 : 6 : 4′ : 5′-dimethylenetetraoxy-2-phenylindazole-2′-carboxylic acid, which on oxidation is converted into 4 : 5 : 4′ : 5′-dimethylenetetraoxyazobenzene-2 : 2′-dicarboxylic acid.

The formation of an unsymmetrical nitro-compound on nitrating azoxypiperonal led to further experiments on the nitration of *azoxyveratrole*, in which it was found that in acetic acid solution only a mononitro-derivative, $C_6H_3(OMe)_2{\cdot}NO{:}N{\cdot}C_6H_2(OMe)_2{\cdot}NO_2$, was formed; similarly, bromination in acetic acid solution gave a monobromo-product, *6-bromoazoxyveratrole*,

$$C_6H_3(OMe)_2{\cdot}NO{:}N{\cdot}C_6H_2Br(OMe)_2.$$

These results accord well with the unsymmetrical constitution of azoxy-compounds as originally suggested by Angeli. D. F. T.

A Method of Formation of 6 : 6′-Dichloro-2 : 2′-azobenzoic Acid. S. Reich and W. Merki (*Bull. Soc. chim.*, 1917, [iv], **21**, 8—13).—When an aqueous alcoholic solution of 6-chloro-2-nitrobenzaldehyde (1 mol.) and potassium cyanide (5 mols.) is acidified at 0° with hydrochloric acid and, after one hour, heated on a water-bath, the *cyanohydrin*, $NO_2{\cdot}C_6H_3Cl{\cdot}CH(OH){\cdot}CN$, a yellow powder, m. p. 134—136°, is obtained. If, however, the acidified mixture is allowed to remain twenty-four hours and then heated on a water-bath with concentrated hydrochloric acid, the product is *6 : 6′-dichloro-2 : 2′-azobenzoic acid*, $CO_2H{\cdot}C_6H_3Cl{\cdot}N{:}N{\cdot}C_6H_3Cl{\cdot}CO_2H$, yellow needles, m. p. 248—250° (decomp.), which, when distilled with calcium oxide, gives 3 : 3′-dichloroazobenzene, m. p. 96°. If the acid is reduced with stannous chloride or with hydrogen in the presence of palladium, a *compound*, $C_{14}H_6O_2N_2Cl_2$, pale yellow needles, m. p. 347—348°, is obtained, to which the constitution (annexed formula) is assigned. The proof of this constitution is given by the following series of reactions. *Ethyl 6 : 6′-dichloro-2 : 2′-azobenzoate*, yel-



low crystals, m. p. 125—126°, when reduced with hydrogen in the presence of palladium, gives *ethyl* 6 : 6′-*dichloro*-2 : 2′-*hydrazobenzoate*, colourless rhombohedra, m. p. 87—88°. When concentrated hydrochloric acid is added to an alcoholic solution of this ester, it yields the cyclic compound, m. p. 347—348°, described above.

W. G.

Azocarboxylic Acids. A. ANGELI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 95—101).—Owing to its analogy in form to nitroxyl, O:NH, the unstable phenyldi-imide, NPh:NH, should exhibit a similar series of reactions. It is, indeed, found that phenyldi-imide reacts readily with aromatic aldehydes, giving compounds of the type of *as.*-benzoylphenylhydrazine: R·CHO + NPh:NH = OH·CR:N·NHPh = R·CO·NH·NHPh. To effect this reaction it is not necessary to make use of the pure phenylazocarboxylate, $NPh:N \cdot CO_2K$ (compare Widman, A., 1895, i, 603), since the liquid obtained by hydrolysing the amide, $NPh:N \cdot CO \cdot NH_2$, with dilute potassium hydroxide at a gentle heat serves equally well. When acetone is used in place of the aromatic aldehyde, no characteristic products are obtained.

This reaction is analogous to some extent with those in which the scission of the benzenesulphonic derivatives of hydrazine or phenylhydrazine take part (A., 1915, i, 847).

Oxidation of phenylazocarbonamide in acetic acid solution by means of hydrogen peroxide yields a *compound*, which forms pale yellow needles decomposing at 151°, and appears to be one of the two azoxy-derivatives, $O:NPh:N \cdot CO \cdot NH_2$ and $NPh:NO \cdot CO \cdot NH_2$, corresponding with the original azo-compound, $NPh:N \cdot CO \cdot NH_2$.

T. H. P.

Formation of *m*-Nitrophenylhydrazine from *m*-Nitroaniline by Bischler and Brodsky's Method. A. W. VAN DER HAAR (*Chem. Weekblad*, 1917, **14**, 147—148).—The low yield of *m*-nitrophenylhydrazine is due to the great solubility of the intermediate products. The difficulty can be overcome by saturating the liquid with sodium chloride.

A. J. W.

Isomeric Hydrazones of Glyoxylic Acid. M. BUSCH, FRIEDR. ACHTERFELD, and RUD. SEUFERT (*J. pr. Chem.*, 1915, [ii], **92**, 1—39. Compare Busch and Meussdörffer, A., 1907, i, 347).—It has already been shown that the *o*-bromophenylhydrazone of glyoxylic acid can exist in two forms (*loc. cit.*), and the authors now describe the conditions under which it is generally possible to favour the formation of either modification of a substituted phenylhydrazone of this acid. The isomeric modifications of any arylhydrazone have very different solubility in benzene, the sparingly soluble variety being described as the α-isomeride and the more soluble as the β-form. If interaction between dichloroacetic acid and the arylhydrazine occurs in presence of alkali carbonate or hydrogen carbonate, the sparingly soluble α-form preponderates in the product, but with an excess of alkali hydroxide the proportion

of the β-compound is greatly increased. Substitution in the meta- or para-position of the phenylhydrazine exerts no important influence on the progress of the reaction, but if the ortho-position is occupied the result shows an increase in the percentage of the β-product. The isomerism of the hydrazones extends to their salts, esters, and benzoyl derivatives, but acetic anhydride appears to exert a disturbing influence on the β-compounds, only one set of acetyl derivatives being obtainable. The β-compounds are more strongly acidic than the α-isomerides, and it appears most probable that the existence of the isomerides is due to stereoisomerism, representable by the formulæ $\begin{array}{c}H\cdot C\cdot CO_2H\\ \| \\ N\cdot NHR\end{array}$ and $\begin{array}{c}H\cdot C\cdot CO_2H\\ \| \\ NHR\cdot N\end{array}$ for the α- and β-compounds respectively. This view explains the relatively greater acidity of the β-isomerides and the favourable influence of hydroxyl ions on their formation; it is also in agreement with the greater stability of the esters of the β-forms.

α-Glyoxylic acid phenylhydrazone, m. p. 138°, has already been obtained by the interaction of dichloroacetic acid and phenylhydrazine in the presence of alkali carbonate (Busch and Meussdörffer, *loc. cit.*; Elbers, A., 1885, 534). In the presence of excess of alkali hydroxide the product contains the former compound accompanied by the β-*isomeride*, yellow needles, m. p. 128—129° (decomp.), which can be separated by its ready solubility in benzene. The β-hydrazone dissolved in methyl-alcoholic sulphuric acid undergoes transformation into the α-isomeride, which further undergoes partial esterification. Both isomerides form salts with alkalis; the α-isomeride yields a *potassium* salt, yellow crystals; a sodium salt, $C_8H_7O_2N_2Na$, colourless leaflets, decomp. near 250°; a sparingly soluble sodium salt, $C_8H_7O_2N_2Na,C_8H_8O_2N_2$; an ammonium salt, $C_8H_7O_2N_2NH_4$, prisms, m. p. near 175° (decomp.), and a sparingly soluble ammonium acid salt, yellow leaflets; the β-isomeride forms a *sodium* salt, $C_8H_7O_2N_2Na$, m. p. indistinct near 273° (decomp.), more soluble than the corresponding salt of the α-compound.

The following phenylhydrazones of glyoxylic acid were prepared in the same manner as the preceding, with the exception that alcohol was added for the purpose of dissolving the arylhydrazine.

Glyoxylic acid m-4-*xylylhydrazone*, $C_6H_3Me_2\cdot NH\cdot N\colon CH\cdot CO_2H$; α-compound, yellow leaflets, m. p. 125—126° (decomp.); β-compound, yellow needles, m. p. 110° (decomp.); the *sodium* salt of each consisted of yellow leaflets; the β-compound could be converted into the α-isomeride by the action of methyl-alcoholic sulphuric acid at the ordinary temperature for four hours. *Glyoxylic acid* m-2-*xylylhydrazone;* α-compound, pale yellow, cubical crystals, m. p. 142—144° (decomp.); β-compound, sulphur-yellow needles, m. p. 115—117° (decomp.). *Glyoxylic acid* ψ-5-*cumylhydrazone*, $C_6H_2Me_3\cdot NH\cdot N\colon CH\cdot CO_2H$; α-compound, yellow leaflets, m. p. 144—145°; β-compound, greenish-yellow needles, m. p. 127° (decomp.). *Glyoxylic acid* o-*chlorophenylhydrazone*; α-form, yellow needles, m. p. 153—154° (decomp.); β-form, m. p. 142—143° (decomp.) (compare Busch and Meussdörffer, *loc. cit.*).

Glyoxylic acid *o*-bromophenylhydrazone in both forms has already been described (Busch and Meussdörffer, *loc. cit.*); the β-form can, as usual, be converted into the α-isomeride by the action of methyl-alcoholic sulphuric acid, the α-isomeride in part undergoing change into its *methyl* ester, needles, m. p. 139°; the α- and β-modifications of the m-*bromophenylhydrazone*, $C_6H_4Br \cdot NH \cdot N:CH \cdot CO_2H$, form yellow leaflets, m. p. 136—139°, and yellow needles, m. p. 122° respectively, whilst the α- and β-isomerides respectively of the p-*bromophenylhydrazone* form yellow needles, m. p. 137° (decomp.) (*benzoyl* derivative, yellow leaflets, m. p. 175—176°), and yellow leaflets, m. p. 121° (decomp.) (*benzoyl* derivative, yellow leaflets or needles, m. p. 123°). *Glyoxylic acid* o-*iodophenylhydrazone*; only the α-form was isolable (Busch and Meussdörffer, *loc. cit.*); p-*iodophenylhydrazone*; α-modification, orange-yellow needles, m. p. 155° (decomp.); β-isomeride, yellow needles, m. p. near 135° (decomp.). *Glyoxylic acid phenylmethylhydrazone*,

$$NMePh \cdot N:CH \cdot CO_2H,$$

was obtained only in one form, probably of the β-constitution, colourless leaflets, m. p. 165—167° (decomp.); the corresponding phenylethylhydrazone (compare Elbers, A., 1885, 534) also was obtained in only one form.

Glyoxylic acid semicarbazone, m. p. 202—203° (compare Darapsky and Prabhakar, A., 1912, i, 841), and pyruvic acid phenylhydrazone appear not to yield stereoisomerides.

The semicarbazones of glyoxylic esters cannot be obtained by the interaction of the arylhydrazine with the alkyl dichloroacetate because of the necessity of the presence of alkali, and, as has been already mentioned, the action of alcohol and mineral acid on the two sets of isomerides yields the esters of the α-modifications only. For the preparation of the β-esters it is necessary to apply the alkyl iodide or the alkyl sulphate, preferably the latter, to an alkaline solution of the corresponding acid. The following methyl esters were prepared: *Methyl glyoxylate phenylhydrazone*, α-form, needles or leaflets, m. p. 137° (compare Harries, A., 1903, i, 605); β-form, yellow crystals, m. p. near 70°. *Methyl glyoxylate* m-4-*xylylhydrazone*, α-form, silky needles, m. p. 142—143°; β-form, pale yellow needles, m. p. 69°. *Methyl glyoxylate* ψ-5-*cumylhydrazone*, α-form, yellow needles, m. p. 175°; β-form, yellow needles, m. p. 86°. *Methyl glyoxylate* p-*bromophenylhydrazone*, α-form, needles, m. p. 191—192°; β-form, leaflets, m. p. 102°. *Methyl glyoxylate phenylmethylhydrazone*, only one form obtained, yellow platelets, m. p. 61—62° (see above).

The esters are more stable than their parent acids. When heated to fusion the α-esters undergo partial transformation into their β-isomerides, a similar equilibrium generally being attained if either modification is kept with methyl-alcoholic sulphuric acid at the ordinary temperature. Concentrated alcoholic hydrogen chloride causes intermolecular condensation, the α-form of methyl glyoxylate phenylhydrazone being converted into *ethyl glyoxylate phenylazoacetylphenylhydrazone*,

$$NPh:N \cdot CH_2 \cdot CO \cdot NPh \cdot N:CH \cdot CO_2Et;$$

orange-red needles, m. p. 154°, with concurrent displacement of the methyl group by ethyl; the corresponding *acid*, $C_{16}H_{14}O_3N_4$, forms orange-coloured needles, m. p. 225° (decomp.). By the action of acetic anhydride and sodium acetate aided by heat, both the α- and β-forms of an ester are converted into the acetyl derivative of the α-isomeride, the phenylhydrazone of methyl glyoxylate yielding an *acetyl* derivative, $C_{11}H_{12}O_3N_2$, colourless needles, m. p. 105°, whilst the stereoisomeric *m*-4-xylylhydrazones give an *acetyl* compound, $C_{13}H_{16}O_3N_2$, colourless needles or prisms, m. p. 88°.

Nitrous acid reacts with the α- and β-forms of glyoxylic acid phenylhydrazone producing benzeneazoformaldoxime (compare Busch and Meussdörffer, *loc. cit.*), whilst with the corresponding esters only the α-isomerides are affected, the product being the expected alkyl arylazoformaldoximecarboxylate; thus the phenylhydrazone of methyl glyoxylate yields *methyl phenylazoformaldoximecarboxylate*, NPh:N·C(:NOH)·CO_2Me, red crystals, m. p. 136°, whilst the *m*-4-xylylhydrazone and ψ-5-cumylhydrazone compounds respectively give rise to red crystals, m. p. 152°, and red needles, m. p. 170°, presumably of the corresponding *oxime* derivatives. Glyoxylic acid phenylmethylhydrazone and its methyl ester are inert towards nitrous acid, but pyruvic acid phenylhydrazone gives phenylazoacetaldoxime with loss of carbon dioxide. The marked difference in behaviour between the α- and β-isomerides of the arylhydrazones of glyoxylic acid discords with the view of their stereoisomeric nature, and is to be examined further.

It was hoped by the action of phenylcarbimide on the isomeric hydrazones to obtain isomeric semicarbazones, of which the relative structure could be clearly distinguished by their chemical properties, especially the ease of ring formation. Unfortunately, however, the arylhydrazones of glyoxylic acid refused to react with phenylcarbimide, and with the methyl esters a definite result was obtained only with the phenylhydrazone compound; in this case the necessary temperature was so high that partial isomerisation occurred; but as the β-isomeride appeared to be unaffected by phenylcarbimide, the resulting *methyl glyoxylate diphenylsemicarbazone*, CO_2Me·CH:N·NPh·CO·NHPh, colourless needles, m. p. 159°, is probably derived from the α-form of the parent ester; the corresponding *glyoxylic acid diphenylsemicarbazone*, $C_{15}H_{13}O_3N_3$, forms colourless needles, m. p. 191°. These products exhibited no tendency to ring formation, either alone or on oxidation, and so furnish slight confirmatory evidence of the structure assumed for the α-isomerides.

In an endeavour to obtain the hydrazones of the anilide of glyoxylic acid, dichloroacetanilide and phenylhydrazine were caused to react in boiling alcoholic solution containing pyridine; the product, however, was phenylazoformaldehyde phenylhydrazone, NPh:N·CH:N·NHPh, probably formed by concurrent oxidation and condensation of phenylhydrazine and the phenylhydrazone of glyoxylic anilide or acid. D. F. T.

Specific Gravity of Aqueous Solutions of Hens' Egg-albumin. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 458—461).—The albumin of hens' eggs represents a saturated solution containing about 15% of the albumin, together with small proportions of fat and salts. At 17°, the saturated solution contains 15·35%. The values of D^{17} for solutions of different concentrations are: 1%, 1·00283; 5%, 1·01341; 10%, 1·02666; 15%, 1·03942. The limiting solubility of albumin being 15·35%, the specific gravities for solutions of higher concentrations (up to 60%) given in Witz's table (*Chemiker-Kalendar*) are without experimental foundation. For 5% solutions, the following results were obtained: (1) untreated egg-albumin, D^{15} 1·01341, $[\alpha]_D$ −36·6°; (2) fat-free albumin, prepared by extraction with light petroleum, D^{15} 1·01314, $[\alpha]_D$ −36·6°; (3) fat- and salt-free albumin, obtained by treating a solution of the fat-free albumin with lead acetate and decomposing the lead albuminate with hydrogen sulphide, D^{15} 1·01288, $[\alpha]_D$ −36·6°. T. H. P.

Legumin as the Analogue of Casein. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 469—470).—Legumin (Merck's) resembles casein in its physical and chemical characters. Contrary to the statement of Osborne and Harris concerning the legumin of horse-beans, it does not dissolve in 10% sodium chloride solution, but it dissolves in water containing 0·5% of hydrochloric acid (1 : 2) and 0·2% of pepsin, its specific rotation in this solution being $[\alpha]_D$ −42·88°. It contains 0·16% of phosphorus, and it gives the following colour reactions, the sensitiveness being indicated in brackets: biuret (1 : 3030), Millon's (1 : 1510), Adamkiewicz's (1 : 14920), Molisch's (1 : 14920), Pettenkofer's (1 : 3030), and Ostromisslenski's (1 : 1510).
T. H. P.

Adenine-uracil-dinucleotide and the Structure of Yeast-Nucleic Acid. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **29**, 111—122).—*Adenine-uracil-dinucleotide* is obtained as an amorphous powder by the action of dilute ammonium hydroxide on yeast-nucleic acid. It is lævorotatory, $[\alpha]_D$ −6·8°, and gives a crystalline *tetrabrucine* salt, $C_{19}H_{25}O_{15}N_7P_2,4C_{23}H_{26}O_4N_2,14H_2O$, m. p. 174—175° (decomp.). On treatment of the dinucleotide with ammonia in an autoclave at 135°, adenosine is liberated, and is isolated as the picrate, m. p. 183·5° (corr.). Uridine is obtained from the filtrate by Levene and La Forge's method (A., 1912, i, 325). The hydrolysis of the dinucleotide with sulphuric acid yields adenine and uracil.

The preparation of the above tetrabrucine salt of the dinucleotide indicates that the two mononucleotide groups are joined to one another, not through their phosphoric acid groups as ordinarily

$$\begin{array}{ll}
O{:}P(OH){\cdot}O{\cdot}C_5H_8O_3{\cdot}C_5H_4N_5 & O{:}P(OH)_2{\cdot}O{\cdot}C_5H_7O_2{\cdot}C_5H_4N_5 \\
\quad | & \qquad\qquad\quad | \\
\quad O & \qquad\qquad\quad O \\
\quad | & \qquad\qquad\quad | \\
O{:}P(OH){\cdot}O{\cdot}C_5H_8O_3{\cdot}C_4H_3O_2N_2 & O{:}P(OH)_2{\cdot}O{\cdot}C_5H_7O_2{\cdot}C_4H_3O_2N_2 \\
\qquad (I.) & \qquad\qquad (II.)
\end{array}$$

represented (I), but through their carbohydrate groups (II). If (I) were correct, only a dibrucine salt could be obtained. It is probable that the same mode of nucleotide linking exists throughout the entire nucleic acid molecule (see next abstract).

H. W. B.

Mode of Nucleotide Linking in Yeast-Nucleic Acid. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **29**, 123—126. Compare preceding abstract).—When adenine–uracil–dinucleotide is heated with dilute sulphuric acid, half of its phosphoric acid is set free rapidly and completely, whilst the remainder is only slowly liberated. This indicates that one purine and one pyrimidine base are present in the molecule (compare Jones, A., 1916, ii, 356). Yeast–nucleic acid behaves in exactly the same way. Since it has been shown that the nucleotides in adenine–uracil–dinucleotide are combined through the carbohydrate groups (*loc. cit.*), it follows that the union of the four nucleotides in yeast–nucleic acid must also occur through the carbohydrate groups. H. W. B.

Significance of the Condition of the Substrate in the Action of Pepsin. III. Pekelharing's Pepsin. W. E. RINGER (*Kolloid Zeitsch.*, 1916, **19**, 253—276).—Little attention has hitherto been given to the condition of the colloidal substrate in enzyme reactions, but the experiments described in this paper show that this factor is of considerable importance. The observations have reference to proteolytic action under the influence of pepsin prepared according to Pekelharing's method. The fact that this pepsin is much more active than other pepsin preparations is considered to be due to its greater degree of purity.

According to cataphoretic experiments in an electrical field, this pepsin affords no evidence of the existence of an isoelectric point, the particles being under proteolytic conditions always negatively charged. When the anode and cathode liquids are separately examined, it is found that the anode portion is much more active as a proteolytic agent, but less rich in protein. This suggests that the pepsin represents a complex (possibly an adsorption compound) in which the enzyme proper is associated with a relatively large quantity of inactive protein.

In the investigation of the dependence of the proteolytic activity of the pepsin on the condition of the substrate, experiments were made with undissolved albumin in which the solvent capacity of the pepsin was determined; further, with dissolved albumin in which the first stage in the proteolytic action was examined, and also with hetero-, proto-, and deutero-albumoses in order to elicit information relative to later stages of the proteolytic series of changes.

The results obtained show that the two first-mentioned processes depend on the condition of the substrate, in that maximum activity of the enzyme corresponds with a maximum in the degree of hydration of the albumin as measured by the swelling of the substrate. According to the results for solutions of different acids, the

sequence of the acids, when arranged according to the activity of the pepsin, is the same as the sequence which gives the acids in the order of their swelling effects. The retarding influence of different salts on the proteolytic activity of the enzyme is also found to run parallel with the influence which these salts exhibit in reducing the swelling of the albumin in acid solution.

In the later stages of the proteolytic series, when the condition of the substrate is subject to relatively less variation, the activity of the pepsin would seem to be affected to a greater extent by other factors, of which the hydrogen-ion concentration is of particular importance. It has, of course, been supposed that this is the main factor in all enzyme reactions of this type, but the facts adduced by the author seem to show that the condition of the substrate is probably of greater importance when the reaction in question is such that considerable variations in the substrate are possible. H. M. D.

A Comparative Study of the Proteolytic Enzymes—Erepsin from the Intestine and Ereptase from Yeast. K. G. DERNBY (*Medd. Nobel Inst.*, 1916, **3**, (14), 1—30).—The conversion of glycylglycine into glycine under the influence of the enzyme erepsin obtained from the duodenum of the pig and of ereptase extracted from yeast press-juice has been examined in a series of experiments.

For both enzymes, the optimum hydrogen-ion concentration at 38° is approximately that corresponding with $p_H = 7 \cdot 8$. If the enzyme concentration relative to that of the dipeptide is sufficiently great, the transformation occurs in both cases in accordance with the equation for a unimolecular reaction. There is, however, a very marked difference between the two enzymes in respect of the effects which are produced by the addition of neutral salts. In the case of ereptase, the influence of added salts is very slight, whereas the rate of hydrolysis by erepsin is greatly reduced when salts are added to the solution. The retarding effect is independent of the nature of the ions, and appears to be determined solely by the total concentration.

Similar experiments on the proteolytic action of the enzymes with polypeptides have shown that the decomposition takes place much more slowly than in the case of glycylglycine. Towards peptone, the two enzymes behave very similarly, but casein is acted on more rapidly by erepsin than by ereptase.

On account of the sensitiveness of erepsin to the influence of neutral salts, ereptase is to be preferred to erepsin for experimental work in the kinetic investigation of proteolytic processes.

H. M. D.

Physiological Chemistry.

The Permeability of Red Blood Corpuscles to Electrolytes. H. Rohonyi (*Koll. Chem. Beihefte*, 1916, **8**, 337—376).—The permeability of red blood corpuscles to electrolytes has been examined in experiments with aqueous solutions of nitrites, chlorates, and ferricyanides, under the influence of which the hæmoglobin is transformed into methæmoglobin. When the blood corpuscles are subjected to the action of solutions of the nitrites, the nitrite ion is absorbed, and this absorption is accompanied by the removal of the chlorine ion from the corpuscles. The chlorine ion re-enters the corpuscles when these are subsequently exposed to the action of a sodium chloride solution. The ionic transfer is independent of the relative magnitudes of the osmotic pressures of the inside and outside solutions. The absorption of the nitrite ion is accelerated by cations and retarded by anions. The retarding influence of the anions decreases in the order: thiocyanate, oxalate, nitrate, iodide and chloride, sulphate. The sequence is independent of the hydrogen-ion concentration of the solutions, but if the solutions are very dilute, the anions increase the rate of absorption of the nitrite ion.

The absorption effects observed with hæmolysed blood and with a solution of crystallised hæmoglobin are almost identical with those found in the experiments with blood corpuscles. This identity was also found in the absorption of the chlorate ion, which only occurs at higher temperatures On the other hand, the ferricyanide ion in neutral solution is absorbed by hæmolysed blood, but not by the corpuscles. In acid solution, ferricyanides cause agglutination, which process takes place previously to the transformation of the hæmoglobin.

From the above observations, the author concludes that blood corpuscles have no specific covering membrane, and that the absorption of ions by hæmoglobin is a process which is fundamentally identical with the absorption of ions by suspended particles and by colloids. H. M. D.

The Action of Carbon Dioxide and Oxygen on the Permeability of Red Blood Corpuscles to Electrolytes. H. Rohonyi and A. Lóránt (*Koll. Chem. Beihefte*, 1916, **8**, 377—390).—Under the influence of carbon dioxide, there is a transference of chloride from the serum to the red blood corpuscles, and at the same time the alkalinity of the serum increases. These changes in the distribution of chloride and alkali between corpuscles and serum are also found when the structure of the corpuscles is destroyed by hæmolysis. It is suggested that the proteins of the red corpuscles under the influence of carbon dioxide react with the sodium chloride, absorbing the chlorine ion and producing sodium carbonate, the presence of which in the serum increases the alkalinity.

A new method for the estimation of the alkali titre of serum and albuminous liquids is described. This method depends on the fact that the proteins are coagulated by potassium ferricyanide when, by addition of acid, the hydrion concentration is raised to a value which differs only slightly from the neutral point. The titration is made with $N/20$-sulphuric acid, and special experiments have shown that the end-point is not affected by the presence of carbonic acid. H. M. D.

Two Peculiarities of Red Blood Corpuscles (Endocoagulation and Reversal of Hæmolysis). H. ROHONYI (*Koll. Chem. Beihefte*, 1916, **8**, 391—398).—If a substance, which coagulates proteins, is added to a suspension of red blood corpuscles, coagulation of the hæmoglobin occurs within the corpuscle. The conditions under which this endocoagulation takes place are nearly the same as those which obtain in the coagulation of hæmolysed blood and of a solution of crystallised hæmoglobin.

The reversal of hæmolysis has been observed on the addition of protein-coagulating substances to a hæmolysed blood solution. This phenomenon and the facts relating to endocoagulation are considered to afford evidence against the view that red blood corpuscles have a covering membrane, the selective permeability of which is supposed to play a considerable part in determining the characteristic properties of the corpuscles. H. M. D.

Cholesterol and Cholesterol Esters in Human Blood. W. R. BLOOR and ARTHUR KNUDSON (*J. Biol. Chem.*, 1917, **29**, 7—13. Compare A., 1916, ii, 650).—A constant relation exists between free cholesterol and cholesterol esters in normal and in most specimens of pathological blood, slight variations occurring only in cases of cancer and nephritis. H. W. B.

Cholesterol in Human Blood under Pathological Conditions. W. DENIS (*J. Biol. Chem.*, 1917, **29**, 93—110).—Estimations have been made of cholesterol in the blood of normal individuals and of a large number of persons suffering from the more common diseases, including nephritis, syphilis, diabetes, typhoid fever, pneumonia, pleurisy, cancer, etc. A slight increase in cholesterol content was noted only in a few of the cases of diabetes. Low cholesterol values do not appear to be characteristic of any special pathological condition other than marked prostration. The author draws the conclusion that cholesterol estimations in blood do not have, at present, any value for clinical diagnosis or prognosis. H. W. B.

Hæmocyanin. CH. DHÉRÉ (*J. Physiol. Pathol. gén.*, 1916, **16**, 985—997. Compare A., 1905, i, 164; 1910, i, 647).—For the estimation of copper in the blood of molluscs and crustacea (present in the respiratory pigment hæmocyanin) the organic matter is destroyed by heating with sulphuric and nitric acids, the copper is

deposited electrolytically on platinum, is dissolved off by nitric acid, and estimated colorimetrically as ferrocyanide. The blood of *Octopus* and of *Sepia* is richest in copper, on the average 23·5 mg. of Cu in 100 c.c. of blood. That of *Homarus vulgaris* contains 10 mg., of *Helix pomatia*, 6·5—7·5 mg. per 100 c.c. A bibliography of forty-six papers is given. G. B.

Feeding Experiments with Deficiencies in the Amino-acid Supply. Arginine and Histidine as possible Precursors of Purines. HAROLD ACKROYD and FREDERICK GOWLAND HOPKINS (*Biochem. J.*, 1916, **10**, 551—576).—When arginine and histidine are together removed from the diet of rats which have been previously growing on a complete amino-acid mixture, there is a rapid loss of body-weight and a decrease in the amount of allantoin excreted in the urine. When the amino-acids are replaced, growth recommences, and the excretion of allantoin returns to the normal. When only one of these acids is withdrawn, loss in body-weight is not observed, and there may even be growth; the fall in urinary allantoin is also slight. Nutritional equilibrium is possible, therefore, in the absence of one of these related amino-acids, but not in the absence of both. The authors suggest that this is because each one of them can, in metabolism, be converted into the other.

The removal of tryptophan from the food produces a nutritional failure, which is even greater than when arginine and histidine are withheld. The absence of vitamines also results in a rapid loss in body-weight. In neither of these cases, however, is there any diminution in the excretion of urinary allantoin. Since allantoin is the end-product of purine metabolism in these animals, the authors consider that arginine and histidine play a special part in purine metabolism, probably constituting, in fact, the raw material (or the most readily available raw material) for the synthesis of the purine ring in the animal body. H. W. B.

Relative Value of Certain Proteins and Protein Concentrates as Supplements to Corn Gluten. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL, with EDNA L. FERRY and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1917, **29**, 69—92).—The authors present data regarding the growth of rats and showing the relative nutritive values of a number of proteins and protein "concentrates" when used to supplement corn gluten in an otherwise adequate ration. The products studied include caseinogen, lactalbumin, edestin, cottonseed protein, soja bean flour, beef, brewer's grains, pea meal, peanut meal, etc. These food materials vary greatly in their efficiency for promoting growth when employed in conjunction with corn gluten; and this variability is dependent primarily on the relative content of lysine and tryptophan. Corn gluten is deficient in these amino-acids, and their addition as such, or in the form of proteins yielding them, renders the corn gluten suitable for promoting growth.

Of the various proteins employed to supplement the inefficient corn gluten, lactalbumin is by far the most effective. Brewers'

grains and distillers' grains are the least effective, presumably on account of their low content of lysine. Evidence is afforded that the small additions of the more efficient proteins actually supplement the corn gluten instead of themselves furnishing all the protein used for growth, in that equivalent amounts of these proteins alone in a similar ration are incapable of inducing a comparable degree of growth. Small amounts of a superior protein are often just as efficient for growth as larger amounts of a less adequate protein. Attention is directed to the probable value of these results in practical animal husbandry. H. W. B.

Growth of Rats on Diets of Isolated Food Substances. THOMAS BURR OSBORNE and LAFAYETTE BENEDICT MENDEL (*Biochem. J.*, 1916, **10**, 534—538).—The authors are in agreement with Drummond (A., 1916, i, 522) that both fat-soluble and water-soluble accessory substances are necessary for growth. H. W. B.

Non-existence of Free or Combined Lecithin in Egg-yolk and in Animal and Vegetable Biological Structures. NICOLA ALBERTO BARBIERI (*Gazzetta*, 1917, **47**, i, 1—37).—The fatty substances of egg-yolk may be completely removed in a pure condition by means of neutral solvents, and on hydrolysis they yield only glycerol and aliphatic acids. These fatty substances may hold, in a state of solution or suspension, nitrogenous or chromatin principles and phosphates which may be removed by either dialysis or hydrolysis with a very dilute acid, or repeated washing with distilled water in presence of alcohol, without the formation of any trace of glycerol from the fatty substances. The whole of the phosphorus of egg-yolk occurs in the form of phosphoric acid combined with potassium, sodium, calcium, and magnesium. In no case can glycerophosphoric acid be obtained by treating the egg-yolk with a neutral solvent, as this compound makes its appearance only after hydrolysis; if the alkali soap is decomposed by means of acid, the glycerol passes into solution, together with the phosphoric acid derived from the phosphates. The conclusion is drawn that the glycerol of the supposed lecithin actually exists in egg-yolk combined with aliphatic acids to form fats. Further, egg-yolk contains no trace of choline, the supposed biological choline being a product either of the degradation of ovochromin or of putrefaction.
T. H. P.

Distribution of Esterases in the Animal Body. AGNES ELLEN PORTER (*Biochem. J.*, 1916, **10**, 523—533).—Enzymes capable of hydrolysing fats and waxes are widely distributed among the organs of man, ox, sheep, pig, cat, rabbit, and guinea-pig. Butyrinase and lecithase are always present, whilst lipases for splitting olein, stearin, and palmitin occur in most organs, particularly in the pancreas and liver. Wax-splitting enzymes are found in several parts of the body besides the skin.

The author directs attention to the fact that those animals which, like the guinea-pig, are very susceptible to tubercle, are compara-

tively poor in esterases, whilst animals, such as the cat, which are seldom attacked by this disease are well provided with them. In all species the lungs are comparatively deficient in esterases.

H. W. B.

Chemical Examination of the Oil from the Australian Dugong. R. W. CHALLINOR and A. R. PENFOLD (*J. Soc. Chem. Ind.*, 1917, **36**, 192—195).—The specimen of oil investigated was obtained from the blubber of a single animal. It was of a pale straw tint, clear and limpid, and without pronounced taste. On keeping, a copious, white, crystalline deposit, consisting of innumerable wheatsheaf-like bundles of needles, separated, which was completely redissolved at 36° and remained in solution for some hours, even when the temperature had fallen below 20°. It had $D^{15.5}$ 0·9161, n^{30} 1·4628, α_D −0·21 (in a 2-dcm. tube), iodine number 84·26, acid number 0·31, free acid as oleic acid 0·15%, saponification number 200·3, unsaponifiable matter 0·61%. The mixed fatty acids had n^{40} 1·4499, D_{15}^{40} 0·8811, D_{40}^{40} 0·8867, m. p. 35—36°, solidifying point 33°, iodine number 66·19, neutralisation number 180·4, mean mol. wt. 310·43, and yielded 0·77% of polybromide insoluble in ether. (The latter forms a white powder, which turns slightly grey on drying at 100°; it darkens a little at 200° and decomposes at 220°.) The acids were separated into solid and liquid portions by the modified Gusserow-Varrentrapp process, the percentage of liquid acids being 65 (iodine number 94·45) and of solid acids 25 (iodine number 4·72). The latter had n^{60} 1·4390, D_{60}^{60} 0·8911, D_{15}^{60} 0·8782, m. p. 51°, iodine number 4·63, neutralisation number 207·49, mean mol. wt. 269·89. The physical constants of the former were n^{30} 1·4567, α_D^{23} −0·18°, D_{15}^{15} 0·8999, iodine number 29·58, neutralisation number 202·37, mean mol. wt. 276·7.

The slight lævorotation of the oil suggests that the unsaponifiable matter is probably cholesterol, more especially as the latter, if present, would find its way into the liquid acids by the usual methods of separation and render them optically active also, which is in accordance with the author's observations. The constants found for the liquid acids indicate that oleic acid is the principal constituent, together with a small amount of a highly unsaturated acid. Further details are promised in a subsequent communication.

H. W.

Action of the Alkaline-earth Chlorides on Urinary Acidity. CHARLES MAYER (*Bull. Soc. chim.*, 1917, [iv], **21**, 19—25).—The ingestion of magnesium chloride, to an extent insufficient to produce colic, causes a marked rise in the acidity-coefficient of the urine, as calculated from the formula $100n/2000(D-1)$, where n is the volume of standard alkali hydroxide required to neutralise the urine, phenolphthalein being the indicator, and D is the density of the urine. This rise in acidity is only accompanied by a very small diminution in the phosphoric acid content of the urine, the two effects being by no means comparable. The author considers that de Jager's explanation as to the rise in acidity (compare A.,

1912, ii, 276) is insufficient, and that the increase is also due to the interaction, in the intestine, of the magnesium chloride with sodium salts of the fatty acids giving insoluble magnesium salts of these acids and sodium chloride. Normally, the sodium salts would be converted into sodium hydrogen carbonate, which would tend to keep the urinary acidity down. W. G.

Excretion of Creatine and Creatinine Parenterally Introduced. J. F. LYMAN and J. C. TRIMBY (*J. Biol. Chem.*, 1917, **29**, 1—5).—Subcutaneous injections of creatine into rabbits and man are followed by increased urinary excretion of creatinine, indicating the occurrence of a transformation of creatine into creatinine in the body. In man, about 4% of the injected creatine is excreted unchanged and 20% transformed into creatinine; the fate of the remainder is not established.

The injection of creatinine does not lead to the excretion of creatine in the urine, but it is pointed out that this does not prove that the change in this direction does not occur. H. W. B.

Sugar Formation. I. Experiments with Glycine, Glycine Anhydride, Aminoethyl Alcohol and Glycolaldehyde. MAX CREMER and RUDOLF W. SEUFFERT, with BERGER, PAPE, and FABISCHE (*Beitr. Physiol.*, 1916, **1**, 255—286; from *Chem. Zentr.*, 1916, ii, 1045).—An account is given of the experimental work of Berger, Pape, and Fabische on the formation of sugar in the phloridzin diabetic organism. Cremer's equation for the degradation of glycine, $4NH_2 \cdot CH_2 \cdot CO_2H = C_6H_{12}O_6 + 2CO(NH_2)_2$, demands the conversion of one and a-half atoms of carbon for each nitrogen atom. This result was obtained in Berger's best experiments with a phloridzin diabetic dog. Pape's experiments confirm this conclusion, but the observed values are lower than the theoretical figures, from which it is inferred that the whole of the neoglucose does not necessarily appear as 'extra' sugar. Administration of glycine anhydride causes the appearance of considerably less 'extra' sugar than that of glycine. This confirms the results of other authors, and shows that a considerable portion of glycine anhydride escapes combustion within the organism or is not degraded beyond the glycine stage. Fabische's experiments were undertaken with the object of establishing the process by which aminoacetic acid is converted into dextrose (compare Schwenken, A., 1914, i, 1156). Aminoacetaldehyde and aminoethyl alcohol, as reduction products, are closely related to glycine. Administration of aminoethyl alcohol to phloridzinised animals caused distinct narcosis and gave variable results for 'extra' sugar, so that a definite conclusion could not be drawn. Subcutaneous injection of glycolaldehyde gave signs of sugar formation, but the animal became ill on the third day. H. W.

Flavine and Brilliant-Green. Powerful Antiseptics with Low Toxicity to the Tissues. C. H. BROWNING, R. GULBRANSEN, E. L. KENNAWAY, and L. H. D. THORNTON (*Brit. Med. J.*, 1917, i, 73—76).—Most antiseptics examined so far act much more

powerfully in water than in blood serum (compare, for example, Bechhold and Ehrlich, A., 1906, ii, 383), but it has now been found that the reverse holds for 2:8-diamino-10-methylacridinium chloride, a substance originally prepared by Benda (A., 1912, i, 651), at Ehrlich's suggestion, as a trypanocide, and known as trypaflavine. This substance, "flavine," kills *Staphylococcus aureus* at 1:20,000 in water containing 0·7% peptone, but at 1:200,000 in blood serum. For *Bacillus coli*, the corresponding dilutions are 1:1300 and 1:100,000. A 0·1% solution has been used clinically with success, and, as regards staphylococci, it is equivalent to 80% phenol. Flavine has a very low toxicity; 300 c.c. of a 1:1000 solution has been given to man intravenously, and phagocytosis is only inhibited by 1:500 solutions. A tabular comparison with other antiseptics is given. G. B.

Radium as a Substitute, to an Equiradio-active Amount, for Potassium in the so-called Physiological Fluids. H. ZWAARDEMAKER and T. P. FEENSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 633—636).—It has been found that the potassium in a Ringer's solution may be replaced by radium without any alteration in the effect which the solution has on the beating of a frog's heart if the quantity of radium is such that its total radio-activity is the same as that of the potassium. In combination with previous observations, these experiments show that the potassium of the normal Ringer's solution may be replaced by rubidium, uranium, thorium, and radium without altering its influence on the cardiac pulsations if the quantities of the several metals are equivalent in radio-active power. H. M. D.

The Salicylates. IV. Salicylate in the Blood and Joint Fluid of Individuals receiving Full Therapeutic Doses of the Drug. R. W. SCOTT, T. W. THOBURN, and P. J. HANZLIK (*J. Pharm. Expt. Ther.*, 1917, **9**, 217—225).—The concentration of salicylate in the blood and joint fluids of rheumatic individuals receiving full therapeutic doses of the drug is approximately the same, namely, 0·02%. The authors were unable to detect free salicylic acid in the joint fluid of individuals suffering with rheumatic fever. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Disinfecting Power of Complex Organic Mercury Compounds. III. Mercuriated Phenols. (WALTHER SCHRAUTH and WALTER SCHOELLER (*Zeitsch. Hyg. Infektkrankh.*, 1916, **82**, 279—288; from *Chem. Zentr.*, 1916, ii, 1054).—The results previously obtained by the authors with the substitution products

of sodium *o*-hydroxymercuribenzoate, $HO \cdot Hg \cdot C_6H_4 \cdot CO_2Na$ (A., 1912, ii, 376), lead to the conclusion that the disinfecting power would be increased by the substitution of the less acidic phenolic hydroxyl for the carboxyl group. Experiments have now been performed with two mercuriated phenols, and also with substances which contain, in addition to one or two hydroxymercuri-groups, halogen, alkyl, or methoxy-groups. The previous observations have been confirmed in all cases, and the influence of the position of the substituent in the benzene nucleus has been investigated. It has been further observed that the relative positions of the hydroxymercuri- and phenolic groups are important. Considerable differences in the disinfecting power of the three isomeric mercuriated cresols have been noticed; the *m*-derivative is most potent, whilst sodium *o*-hydroxymercuriphenoxide is more active than the isomeric para-compound. In the case of sodium dihydroxymercuriphenoxide (providol), it is shown that the entrance of a second hydroxymercuri-group into the benzene nucleus considerably increases the disinfecting power. The substances were prepared by treating the phenol with mercuric acetate in alcoholic solution; the recrystallised products were dissolved in the calculated amount of sodium hydroxide and diluted with water to the required mercury content. Among the preparations examined, sodium *o*-chlorohydroxymercuriphenoxide and sodium dihydroxymercuriphenoxide have been found particularly active. Their practical importance is increased by the fact that their disinfecting power, in contrast to that of all previously investigated compounds, is not diminished in the presence of soap, and that they are permanently unchanged in soaps which consist chiefly of the sodium salts of saturated fatty acids. Medical preparations of this kind (apidol- and providol-soap) keep well. H. W.

Effect of Phosphorus on Lucerne and Lucerne Bacteria. H. W. Truesdell (*Soil Sci.*, 1917, **3**, 77—98).—Pure cultures of *Bacillus radicicola* from lucerne were inoculated into sterilised soil to which phosphates had been added in the form of di-potassium, di-sodium, and di-calcium phosphates. Bacterial counts were made after seven and fourteen days, and in every case the numbers were larger where phosphate had been present than in the control cultures, the maximum increase in each case being 600% with di-potassium, 100% with di-sodium, and 15% with di-calcium phosphate.

At the same time, lucerne was grown in pot cultures. Unsterilised soil was used, both uninoculated and inoculated with *B. radicicola*, and with and without di-calcium phosphate. The phosphate appeared to stimulate the plants, especially during the seedling stage; it also encouraged nodule formation and increased the dry weight and nitrogen content of the plant. The author is of opinion that the phosphorus acts by a direct stimulation of the living cells, and more especially of those of the nodule bacteria.

L. M. U.

Influence of Salts on the Bacterial Activities of the Soil. J. E. GREAVES (*Soil Sci.*, 1916, **2**, 443—480).—A series of ammonification tests was carried out with soil containing 2% of dried blood, to which were also added the following salts: chlorides, nitrates, sulphates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron. The salts were all added in fractions of their molecular weights, varying from 156×10^{-7} to 10×10^{-3} per 100 parts of soil, so that the results were strictly comparable. With nearly all the salts, some stimulation was obtained at the low concentrations, but beyond a certain point, increasing amounts of the salts gradually inhibited ammonification. The only salts which had an inhibitive effect in all concentrations were calcium chloride and nitrate, potassium chloride and sulphate, sodium sulphate and magnesium nitrate; calcium and magnesium carbonates, on the other hand, never produced any but stimulating effects, even in the highest concentrations. In a general way, it may be said that the acid radicle, rather than the metal, played the more important part in controlling the rate of ammonification, and that the order of decreasing toxicity amongst the salts was usually: chlorides, nitrates, sulphates, carbonates.

The results are also considered in relation to those obtained by Harris (A., 1915, i, 1091) on the effect of salts on the germination and growth of plants. Very similar quantities of the various salts are required to reduce plant growth to half its normal amount or to reduce ammonification by 50%. The author considers the increased osmotic pressure exerted by added salts to be an important factor in retarding bacterial activity in the soil, but he states that it is not the only one. L. M. U.

Biological Changes in Soil during Storage. F. E. ALLISON (*Soil Sci.*, 1917, **3**, 37—62).—A bacteriological study of soil samples was made immediately they were brought into the laboratory and after intervals of storage varying from two hours to eighteen or even sixty days. During the winter months the number of bacteria was much affected by the warmer temperature of the laboratory. In the first twenty-four hours the numbers fell, then rose to a maximum, after which a decline set in until the fourth day, followed by a very gradual rise, which was still apparent when the experiment was stopped on the eighteenth day. During the first day an interval of two hours might cause a change in numbers amounting to 30—40%. In the summer months the change in the numbers during the first few hours of storage was much less marked, and the subsequent decrease was considerably slower. Ammonification, nitrification, and nitrogen fixation were also determined, and fungi were counted in the summer tests. Ammonification varied very much, as did the bacterial numbers. L. M. U.

Ammonifiability versus Nitrifiability as a Test for the Relative Availability of Nitrogenous Fertilisers. C. B. LIPMAN and P. S. BURGESS (*Soil Sci.*, 1917, **3**, 63—75).—Nitrification and ammonification tests were carried out on the following

nitrogenous manures: dried blood, high grade tankage, steamed bone meal, cottonseed meal and fish guano. For the ammonification tests each manure was mixed with each one of twenty-three selected soils at the rate of 2% of the soil, and incubated for seven days. For the nitrification tests each manure was mixed with each soil at the rate of 1% of the soil and incubated for four weeks. At the end of the incubation period ammonia and nitrates were determined.

The availability of the nitrogen as measured by these two methods gave absolutely different and frequently opposite results. Given the fact that plants usually prefer nitrates to ammonia as a source of nitrogen, the authors consider nitrification rather than ammonification to be the more trustworthy test of the availability of nitrogen in a manure. L. M. U.

Nature of Nitrification and Ammonification. K. MIYAKE (*Soil Sci.*, 1916, **2**, 480—492).—It is found that in experiments on ammonification and nitrification, if the rates of increase of ammonia and nitrate are plotted in a curve, the curve is very similar to that of autocatalytic chemical reactions in which one of the products of reaction accelerates the reaction. The maximum increase of ammonia and nitrate per unit time occurs when the total production is half complete, and the processes take place according to the formula $\log x/(A-x)=K(t-t_1)$, where x is the amount of ammonia and nitrate which has been produced at time t, A is the total amount of ammonia and nitrate produced during the process, K is a constant, and t_1 is the time at which half of the total amount of ammonia and nitric acid is produced. L. M. U.

Colouring Matter of Red Torulæ. ALFRED CHASTON CHAPMAN (*Biochem. J.*, 1916, **10**, 548—550).—The absorption spectrum of the colouring matter extracted by chloroform or carbon disulphide from red torulæ differs considerably from that of carrotene. The colouring matter of the torula consists, therefore, of some other substance than carrotene or of a mixture of carrotene with some other colouring matter. H. W. B.

Influence of Certain Organic Substances on the Development of Plants. I. G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 3—7).—In view of the fact that the accessory substances of vegetable organisms, such as glucosides, alkaloids, colouring matters other than chlorophyll, etc., are regarded by some authorities as reserve food materials and by others as excretory products, the authors, who favour the former view, have investigated the influence of certain of these substances on the development of plants.

When an organic compound is introduced into an adult plant either by way of the roots or by inoculation into the stem, no apparent external change is produced, provided that the nature and amount of the substance are such that the plant remains alive.

The germination of beans and maize on cotton-wool is almost completely inhibited by watering with 0·1% mandelonitrile solution, whereas when an amygdalin solution of corresponding concentration (0·55%) is used, all the seeds germinate like those treated with water. If, however, the mandelonitrile is first administered some days after germination, the plants develop, although comparatively slowly, the height attained being less and the root-growth not so marked; on the other hand, the stems are thicker and the plants more robust, since they are able to live through the winter, whilst those provided with complete nutriment dry up in October. That these plants treated with mandelonitrile are nourished at the expense of the nitrogen of this compound whilst the benzaldehyde undergoes oxidation or other transformation, is shown by the absence of hydrocyanic acid or benzaldehyde, even after the extract of the plant has been treated with emulsin.

Hydrocyanic acid in 0·1% concentration retards or prevents the germination of beans and maize, and those plants (about 30%) which grow very soon die. Nicotine tartrate solution containing 0·1% of the alkaloid behaves similarly towards the seeds, and even when it is first applied subsequently to the germination, the plants grow slowly and abnormally. Strychnine tartrate of similar concentration has no apparent influence on the germination of the seeds, but the plants dry up after a few days. The action of caffeine or morphine is similar to that of strychnine. T. H. P.

Pectic Substances of Plants. SAMUEL BARNETT SCHRYVER and DOROTHY HAYNES (*Biochem. J.*, 1916, **10**, 539—547).—The authors describe a method for the preparation of the pectic substances of plants, in which the essential operation is the extraction of the residue, obtained after the expression of the juice, with a warm 0·5% ammonium oxalate solution. A substance of acidic character is thereby obtained from turnips, strawberries, rhubarb, and apples, which is soluble in water and is designated *pectinogen*. On keeping in alkaline solution at the ordinary temperature, pectinogen undergoes conversion into *pectin*, $C_{17}H_{24}O_{16}$, which is also of acidic character and is precipitated from its alkaline solution by acids as a gel insoluble in water.

An aqueous solution of pectinogen does not yield a precipitate when treated with a dilute solution of a calcium salt. Pectin, on the contrary, when dissolved in alkali and then neutralised, gives a gelatinous precipitate with calcium chloride. Addition of strong sodium hydroxide to pectin solutions also yields a gelatinous precipitate.

On distillation with hydrochloric acid, pectinogen yields furfuraldehyde in such a quantity as to indicate that one pentose group is contained in each molecule of pectinogen. H. W. B.

Estimation of Hydrocyanic Acid and the Probable Form in which it Occurs in Sorghum vulgare. J. J. WILLAMAN (*J. Biol. Chem.*, 1917, **29**, 25—36).—In most cases, distillation of sorghum leaves with 5% tartaric acid yields less hydrocyanic acid

than is obtained when the macerated leaves are first allowed to undergo autolysis and are then subjected to the distillation process. In some cases the latter method of treatment yields hydrocyanic acid, whilst a similar sample treated by the first method, especially if it is ground with the tartaric acid solution before distillation, fails to indicate the presence of any acid. The author finds that amygdalin is not hydrolysed by 5% tartaric acid solution, and, relying on the resemblance between amygdalin and the glucoside, dhurrin, present in sorghum leaves, draws the conclusion that hydrocyanic acid is usually present in sorghum, not only in glucosidic combination, but also in another undetermined form.

Hydrolysis of the dhurrin in sorghum by the glucosidase present in the same tissues takes place very rapidly at 45°, but it is entirely prevented if the tissues are first macerated with 5% tartaric acid. Even in the presence of tartaric acid, retention of hydrocyanic acid by the tissues occurs during distillation, and this retention is not appreciably lessened by distilling under reduced pressure. H. W. B.

Effect of Anæsthetics and of Frosting on the Cyanogenetic Compounds of Sorghum vulgare. J. J. WILLAMAN (*J. Biol. Chem.*, 1917, **29**, 37—45. Compare preceding abstract).—Sorghum leaves exposed for a few days to the vapour of chloroform, ether, or alcohol, yield more hydrocyanic acid, both glucosidic and non-glucosidic, than the normal leaves. The author suggests that the anæsthetic stimulates both the hydrolytic and the synthetic actions of the cyanogenetic enzymes. An enzymic powder prepared from the chloroformed leaves is about twenty-five times as active towards amygdalin as a similar powder prepared from normal leaves.

Leaves subjected to a low temperature also contain more glucosidic and non-glucosidic hydrocyanic acid than ordinary leaves. Confirmation is thus furnished of the well-known statement that sorghum is especially poisonous after a frost. H. W. B.

Physical Chemistry of Foods. II. Reduction of the Acidity of Wine with Calcium Carbonate (Chaptalising). Tartaric Acid and its Salts. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1915, **21**, 542—559. Compare A., 1915, ii, 590).—With the object of placing the process of deacidifying wines by means of calcium carbonate on a scientific basis, the author has studied in great detail the physico-chemical properties of tartaric acid and its sodium, potassium, calcium, and barium salts. The investigation has led to the following results: Since the acidity of a wine is defined as its hydrogen-ion content, it follows that the deacidifying constitutes a reduction of the hydrogen-ion concentration. In this process, the chemical equilibrium between normal calcium tartrate and tartaric acid, as well as that between calcium carbonate and tartaric acid, is the controlling factor. The solubility of calcium tartrate in carbon dioxide-free distilled water at 18° is 0·3802 gram per litre, that is, 0·001462 gram-mol. per litre. In distilled water which contains the equilibrium quantity of carbon dioxide the solubility is greater, amounting to 0·4096 gram = 0·001575 gram-mol. per litre at 18°. The equivalent con-

ductivity of normal calcium tartrate and disodium and dipotassium tartrates has been measured down to $v=40,000$. The migration velocity of the secondary tartrate ion ($\frac{1}{2}C_4H_4O_6''$) has been calculated and found to be 55·6 at 18°. The depression of the solubility of calcium tartrate by calcium chloride and by potassium tartrate has been determined, and the degree of dissociation calculated, and values obtained which agree well with those obtained from the electrical conductivity measurements. The solubility product of normal calcium tartrate at 18° has the value $0{\cdot}77 \times 10^{-6}$. The acidity of tartaric acid solutions (1—16 per 1000) was determined by the sucrose inversion method, and values obtained which agree well with those obtained from the conductivity measurements. An addition of 80 grams of ethyl alcohol per litre exercises a considerable influence on the various equilibria existing in the solutions of tartaric acid and calcium tartrate, and consequently the alcohol content of wines must be taken into account when deacidifying with calcium carbonate. During the deacidifying of aqueous solutions of tartaric acid by calcium carbonate, the acidity decreases more rapidly at first than later for equal additions of calcium carbonate. The content of titratable acid, on the contrary, decreases regularly and in proportion to the amount of carbonate added. The same results are obtained during the deacidifying of natural wines, although the decrease in acidity is not at first quite so marked as in the case of aqueous solutions of tartaric acid. This is due to the earlier precipitation of normal calcium tartrate, since, generally, the wine already contains some calcium tartrate, and the presence of alcohol diminishes its solubility, and, further, wine contains other weak acids. The deacidifying of wine by calcium carbonate is therefore not a simple neutralisation. The addition of calcium carbonate brings about a change in the constitution and a marked shifting of the equilibria.

J. F. S.

The Influence of Various Cations on the Rate of Absorption of Ammonium Ion by Soil. K. Miyake (*Soil Sci.*, 1916, **2**, 583—588).—A study of the rate of absorption of the ammonium ion by a soil from an $N/10$-solution of ammonium chloride alone or in the presence of $N/100$-, $N/20$-, or $N/10$-solutions of either sodium, potassium, magnesium, calcium, or aluminium chlorides. The results show that the relation between the time of contact of the soil and the solution and the amount of ammonium ion absorbed can be expressed by the equation $x=Kt^m$ (compare Cameron and Bell, U.S.A. Dep. Agr. Bur. Soils Bull., 30). The rate of absorption of ammonia from ammonium chloride is decreased by the presence of other chlorides, the retardation varying with the chloride present, and increasing with the concentration of the chloride. The retarding effect of the salts used increases in the order $Na < Mg < Ca < Al < K$. The acceleration of the retardation with increasing concentration is positive in the case of sodium, magnesium, and calcium chlorides, and negative in the case of aluminium and potassium chlorides.

W. G.

Ferrification in Soils. P. E. Brown and G. E. Corson (*Soil Sci.*, 1916, **2**, 549—573).—In the first part of the paper an account is given of various methods which were tried for estimating the amount of ferrous iron in soils. None of these were successful, the results showing that ferrous compounds are adsorbed by the soil, and that organic matter, if present in any appreciable quantity, will cause an oxidation as well as a reduction of the iron compounds. Determinations were then made of what the authors call the "ferrifying power" (power of oxidising ferrous compounds) of various soils, this being the difference in the iron rendered soluble in 100 c.c. of sterile water plus 0·1 gram of ferrous carbonate after inoculation with an infusion of the soil and with a sterile infusion of the soil respectively, and incubation for varying periods of time. The results obtained show that the ferrification or deferrification, whilst common to the soils studied, depends on several factors, such as organic content of the soil, cultivation, moisture, etc. No definite correlation with any of these factors was found, but the cultivated soil had the greatest ferrifying power. Experiments conducted with pure cultures of bacteria and moulds show that the common soil organisms and moulds, as well as the iron bacteria, are capable of oxidising ferrous iron. W. G.

The Organic Matter of the Soil. II. A Study of Carbon and Nitrogen in Seventeen Successive Extracts; with some Observations on the Nature of the Black Pigment of the Soil. Ross Aiken Gortner (*Soil Sci.*, 1916, **2**, 539—548).—A continuation of previous work (compare *ibid.*, 1916, **2**, 395). A silt loam soil was extracted with 1% hydrochloric acid until the filtrate no longer contained calcium, and it was then extracted nine times consecutively with fresh quantities of 4% sodium hydroxide solution, and then six times with 0·15% sodium hydroxide solution, the soil residue being dried and analysed. The first six extractions with 4% sodium hydroxide removed relatively more nitrogen than carbon from the soil, but the next nine extractions (three with 4% and six with 0·15% sodium hydroxide) removed relatively more carbon than nitrogen. The C/N ratio of the soil residue was much higher than that of the original soil. The work confirms the earlier observation that the black soil pigment is not soluble in 4% sodium hydroxide solution. It is, however, soluble in the 0·15% solution, from which it is precipitated either by the addition of sufficient sodium hydroxide to bring the strength of the solution up to 4%, or by the addition of salts of the heavy metals, or by acidifying the solution. The pigment cannot be dialysed, and forms a stable ammonium compound soluble in water, which is obtained by evaporating its ammoniacal solution to dryness. Attempts to prepare the pigment in a pure state were unsuccessful, the two preparations made containing, respectively, 37·47% and 51·17% of ash. The composition of the first sample, calculated on an ash-free basis, was C 61·3%; H 4·3%; O 31·6%; N 2·8%. W. G.

Organic Chemistry.

Cuprous *iso*Butylxanthates. RICARDO MONTEQUI DIAZ DE PLAZA (*Anal. Fis. Quim.*, 1917, **15**, 54—60).—*Cuprous isobutylxanthate*, prepared from cupric sulphate and potassium *iso*butylxanthate, has a canary-yellow colour. When heated, it is decomposed, with formation of cupric sulphide. Its yellow solution in chloroform becomes red on warming, but the original colour is restored as the temperature falls. Pyridine transforms the salt into the red modification, which then dissolves. It is unaffected by cold, dilute hydrochloric acid, and only slightly attacked by the hot acid.

When the cupric sulphate is first reduced to the cuprous salt by means of sodium hyposulphite, the red form of the xanthate is produced. It is amorphous, and insoluble in water. Its alcoholic solution changes to the yellow modification, the same transformation being effected by acetone, benzene, carbon disulphide, and chloroform, and by heat. Dilute acids have no action on it, but hot, concentrated hydrochloric acid transforms it into the yellow modification.

It is suggested that the yellow variety has the double formula $(C_5H_9OS_2)_2Cu_2$, and the red modification the simple formula $C_5H_9OS_2Cu$. A. J. W.

The Effect of Heat and Oxidation on Linseed Oil. JOHN ALBERT NEWTON FRIEND (T., 1917, **111**, 162—167).—When linseed oil is "thickened" by heat without appreciable oxidation, an increase is generally observed in the density and viscosity, whilst the coefficient of expansion undergoes a slight decrease; these results are probably due to polymerisation (compare Morrell, A., 1915, i, 75), the molecular weight of the "thickened" oil in benzene being greater than that of the original oil. It is worthy of note that the apparent molecular weight in benzene increases on dilution both for the raw and the heated oil.

Examination of linseed oil at various stages of oxidation between the raw oil and solid linoxyn several months old shows that there is a steady increase in density, but that the volume and weight both attain a maximum, although not simultaneously. The increase in weight at any time is not equivalent to the oxygen absorbed, because volatile matter is lost during the oxidation.

D. F. T.

An Isomeride of Glycuronic Acid. M. L. SAUREZ (*Chem. Zeit.*, 1917, **41**, 87).—An acid is obtained from lemon pulp which yields a soluble barium salt having the formula $Ba(C_6H_9O_7)_2$; this salt when heated with concentrated barium hydroxide solution forms an insoluble yellow salt. The solution gives many of the reactions of glycuronic acid, but no compound is formed with

p-bromophenylhydrazine; the acid radicle could not be converted into glycuronic anhydride. The new acid yields mucic acid on oxidation, and is evidently an isomeride of glycuronic acid.

W. P. S.

Crystallisation and Complementary Properties of the Galactobiose previously obtained by Biochemical Synthesis. EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1917, **164**, 443—445. Compare A., 1916, i, 596).—Galactobiose has now been obtained in a crystalline form, the viscous deposit obtained from its solution in methyl alcohol on the addition of anhydrous ether having spontaneously crystallised after five months. The sugar was obtained in little spherical masses, with a taste slightly sweeter than that of lactose. Dried at 110° for one hour, it had $[\alpha]_D^{16}+53{\cdot}05°$ and showed mutarotation, the results indicating that the product crystallising from methyl alcohol was in the *α*-form. The reducing power of galactobiose is 53·6% that of galactose.

W. G.

Biochemical Synthesis, by means of Emulsin, of a Second Galactobiose. ÉM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1917, **164**, 521—523).—From the residues from the preparation of the galactobiose previously described (compare A., 1916, i, 596; preceding abstract), by extraction with alcohol and subsequent recrystallisation from methyl alcohol, a second galactobiose has been obtained crystallising in microscopic needles, forming stellate clusters. After drying over sulphuric acid in a vacuum, it loses 13·63% of its weight at 110°, indicating the presence of 2MeOH of crystallisation. It softens at 147·5° (corr.) and has m. p. 180° (corr.). It shows mutarotation and has $[\alpha]_D +35{\cdot}01°$, after drying at 110°. Its reducing power is 50·3% of that of galactose. It gives an *osazone*, yellow needles, m. p. 194°. It is hydrolysed in aqueous solution by sulphuric acid and by emulsin.

W. G.

Derivatives of Rhodeose (Degradation of Rhodeose). EMIL VOTOČEK (*Ber.*, 1917, **50**, 35—41).—In the main, an account of the preparation of the oximes of rhodeose and fucose, the acetylation of these, and the subsequent degradation to tetroses by Wohl's method.

Rhodeosoxime, $OH{\cdot}CHMe{\cdot}[CH{\cdot}OH]_3{\cdot}CH{:}N{\cdot}OH$, has m. p. 188—189°, $[\alpha]_D +13{\cdot}2°$, and *fucosoxime* the same m. p. and $[\alpha]_D -12{\cdot}7°$. *iso*Rhodeose does not react with hydroxylamine. The oximes are acetylated by adding them to a boiling mixture of acetic anhydride and sodium acetate, whereby *tetra-acetylrhodeononitrile*, $CH_3{\cdot}[CH{\cdot}OAc]_4{\cdot}CN$, and *tetra-acetylfucononitrile* are formed as very similar, crystalline substances, m. p. 177—178°. A small amount of *tetra-acetylrhodeosoxime acetate*,

$$CH_3{\cdot}[CH{\cdot}OAc]_4{\cdot}CH{:}N{\cdot}OAc,$$

m. p. 115—116°, is formed at the same time; this yields methylfurfuraldehyde on distillation with hydrochloric acid (naphtharesorcinol gives a brilliant magenta coloration with the vapours),

whereas the nitrile gives hydrogen cyanide salts on boiling with 20% potassium hydroxide or ammoniacal-alkaline silver nitrate. If the tetra-acetylrhodeononitrile is treated with ammoniacal silver oxide by Wohl's method, the diacetamide *compound* of rhodeotetrose, $C_9H_{18}O_5N_2$, m. p. 233° (decomp.), is formed. This may be hydrolysed to the rhodeotetrose, the p-*bromophenylosazone* of which crystallises in yellow, cell-like structures, m. p. 143—144° (decomp.).

Rhodeose and fucose react with diphenylmethanedimethyldihydrazine (von Braun, A., 1910, i, 524), but *iso*rhodeose does not. The *hydrazones*, $CH_2[C_6H_4{\cdot}NMe{\cdot}N{:}CH(CH{\cdot}OH)_4{\cdot}CH_3]_2$, are both pale yellow, crystalline powders which melt and decompose at 218° and 221° respectively. J. C. W.

Behaviour of Sugars towards Diphenylmethanedimethyldihydrazine. J. von Braun (*Ber.*, 1917, **50**, 42—43).—The previous experience of aldehydic pentoses and hexoses, coupled with Votčoek's (preceding abstract), gives the author reason to suggest that diphenylmethanedimethyldihydrazine is a very useful agent for the determination of the configuration of the aldoses. Hydrazones are produced by ribose, lyxose, arabinose, rhamnose, rhodeose, fucose, mannose, and galactose, but not by xylose, *iso*rhodeose, or dextrose, the feature common to the former class being that at least two of the three ·CH·OH groups following the aldehyde group have the same spatial arrangements. J. C. W.

Reaction between Starch and Formaldehyde, and the Supposed Diastatic Properties of Formaldehyde. Wilhelm von Kaufmann (*Ber.*, 1917, **50**, 198—202. Compare Woker, this vol., i, 61).—A severe criticism of the experiments on which Woker based her assumption that formaldehyde could imitate diastase in its hydrolysis of starch. The evidence was to the effect that in the presence of formaldehyde (the concentration was as much as 190 times that of the starch) starch soon lost its power of giving a blue colour with iodine. It is now stated that this is obviously due to the well-known fact that starch and formaldehyde combine (compare Syniewski, A., 1903, i, 68), for it is only necessary to remove the aldehyde by boiling, or to fix it by ammonia, or to hydrolyse the compound by adding an acid, to restore the starch completely. No fermentable sugar is formed and no change in rotation occurs. J. C. W.

Identity of the Synthetic Humin Substances with the Natural Humin Substances. L. C. Maillard (*Ann. Chim.*, 1917, [ix], **7**, 113—152).—A theoretical paper in which the author, by a comparative study of the humin substances synthesised from reducing sugars and amino-acids (compare A., 1916, i, 597) and the natural humin substances, endeavours to establish their identity. W. G.

Explosive Peroxide Derivative of Hexamethylenetetramine. A. Leulier (*J. Pharm. Chim.*, 1917, [vii], **15**, 222—229).—When a mixture of 140 grams of hexamethylenetetramine, 140

grams of concentrated nitric acid, and 1220 grams of hydrogen peroxide is kept at 20° to 25° for four hours, a crystalline precipitate separates, which, when dry, is very explosive; it contains carbon 10%, hydrogen 10·06%, oxygen 45·50%, and nitrogen 10%, which composition would correspond with the formula

$$NH(CH_2{\cdot}CH_2{\cdot}O{\cdot}OH)_2.$$

The substance is similar to the peroxide derivative prepared by Girsewald (A., 1912, i, 835), but differs in that it contains only 1 atom of nitrogen in its molecule. W. P. S.

Acylation of Ethyl β-Aminocrotonate and Analogous Compounds. II. ERICH BENARY, FRITZ REITER, and HELENE SOENDEROP (*Ber.*, 1917, **50**, 65—90. Compare A., 1909, i, 888).—In the earlier paper it was shown that ethyl β-aminocrotonate gives two *N*-acyl compounds when treated with either acetyl or benzoyl chloride, but that a derivative in which the acyl group is attached to carbon is formed in the case of chloroacetyl chloride. It would appear, therefore, that the strength of the acid has some influence on the reaction, and so the experiments have been extended to other acyl chlorides and to compounds analogous to ethyl β-aminocrotonate. The reaction is often difficult to explain, however, and no generalisations can yet be made. It is unsafe to predict whether the entering group will be attached to carbon or nitrogen, and at present it is necessary to prove the constitution of the product in each instance.

m-Nitrobenzoyl chloride reacts with the ester in the presence of pyridine to form *α-ethyl β-*m*-nitrobenzoylaminocrotonate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et,$$

in hexagonal prisms, m. p. 150°, which changes into the *β-isomeride*, glistening leaflets, m. p. 74°, when dissolved in acetyl chloride and then reprecipitated by pouring into ice-cold sodium carbonate. The corresponding *ethyl β-*p*-nitrobenzoylaminocrotonates* are: α-, glistening leaflets, m. p. 145°; β-, needles, m. p. 126°. These yield the corresponding nitrobenzamides on boiling with dilute sulphuric acid, which proves the mode of attachment of the acyl group. *o*-Nitrobenzoyl chloride and *o*-bromobenzoyl chloride yield the benzamides at the outset, and *p*-bromobenzoyl chloride gives *p*-bromobenzoic anhydride.

o-Acetoxybenzoyl chloride gives no definite result, and 3:5-dibromosalicyl chloride only forms a *dibromosalicylide*,

$$(C_7H_2O_2Br_2)_n,$$

m. p. 316°. This is really formed by the action of the pyridine alone, but dimethylaniline does not produce it. It is not identical with the dibromosalicylide described by Anschütz and Robitsek (A., 1906, i, 503) or that mentioned by Earle and Jackson (*ibid.*, 177).

Cinnamoyl chloride gives, in the presence of pyridine, *ethyl β-cinnamoylaminocrotonate*, in pale yellow, quadratic prisms, m. p. 154°, which forms a very stable *dibromide*, hexagonal prisms, m. p. 155°, and yields the known γ-aceto-β-phenylbutyric acid, or

occasionally cinnamic acid, on boiling with hydrochloric acid, evaporating to dryness, and triturating with sodium carbonate solution (evolution of ammonia). This α-ester is not changed by acetyl chloride, but a *β-isomeride*, m. p. 96°, is obtained by the action of ethyl cinnamate on ethyl sodioaminocrotonate. $\alpha\beta$-Dibromo-β-phenylpropionyl chloride, m. p. 91°, only gives the corresponding propionamide.

Ethyl chloro-oxalate forms *ethyl γ-amino-α-keto-Δ^{β}-butene-$\alpha\beta$-dicarboxylate*, $NH_2{\cdot}CMe{:}C(CO_2Et){\cdot}CO{\cdot}CO_2Et$, which crystallises in hexagonal prisms, m. p. 87° (decomp.), and is hydrolysed by N-sodium hydroxide in the cold to the *acid ester* (*β-amino-α-ethoxalylcrotonic acid*), $NH_2{\cdot}CMe{:}C(CO_2H){\cdot}CO{\cdot}CO_2Et$, m. p. 124° (decomp.), the *copper* salt of which is pale green, crystallises with $2H_2O$ and decomposes at 213°. If these esters are boiled with phenylhydrazine and alcohol, the *pyrazole* derivative,

$$NPh{<}\begin{matrix} CO{\cdot}CH{\cdot}CMe{:}N{\cdot}NHPh \\ N{=}C{\cdot}CO_2Et \end{matrix}, \text{ or } NPh{<}\begin{matrix} CO{\cdot}CH{\cdot}C(CO_2Et){:}N{\cdot}NHPh \\ N{=}CMe \end{matrix},$$

is formed, as a pale yellow substance, m. p. 147°, which may be hydrolysed by boiling N-sodium hydroxide to the free *acid*, m. p. 253°, the phenylhydrazine salt of which crystallises in slender needles, m. p. 129°. A different product is obtained if the phenylhydrazine is applied in 50% acetic acid solution, namely, *ethyl 1-phenyl-4-α-aminoethylidenepyrazol-5-one-3-carboxylate*,

$$NPh{<}\begin{matrix} CO{\cdot}C{:}CMe{\cdot}NH_2 \\ N{=}C{\cdot}CO_2Et \end{matrix},$$

which crystallises in orange-yellow needles, m. p. 219° (decomp.). This is hydrolysed by boiling N-sodium hydroxide to *4-acetyl-1-phenylpyrazol-5-one-3-carboxylic acid*, m. p. 242° (decomp.), which behaves on titration and towards ferric chloride as an enol, forms a *product* with phenylhydrazine (2 base : 1 acid), m. p. 190°, and yields a *compound*, leaflets, m. p. 169°, when heated above its m. p.

The N-substituted ester isomeric with the above dicarboxylate is formed when ethyl oxalate is added to a suspension of ethyl sodioaminocrotonate in ether. *Ethyl β-ethoxalylaminocrotonate*, $CO_2Et{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et$, crystallises in rhombic platelets, m. p. 60°, and yields the phenylhydrazide of oxamic acid, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NHPh$, on warming with phenylhydrazine and 50% acetic acid. The corresponding *acid ester* (*ethyl β-carboxalylaminocrotonate*, $CO_2H{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et$) is found in the ethereal mother liquor from the above ester, and it may also be obtained from the ester by hydrolysis with alcoholic potassium hydroxide. It crystallises in colourless needles, m. p. 107°, and forms a *compound* with phenylhydrazine (1 : 1), m. p. 146°.

The acylacetonamines were chosen as compounds related to ethyl aminocrotonate for further studies on the action of acyl chlorides in the presence of pyridine. The following derivatives of β-amino-Δ^{α}-propenyl methyl ketone (acetylacetonamine) have been obtained

in this way: the N-*benzoyl* derivative, CH_3·CO·CH⁚CMe·NHBz, large prisms, m. p. 82° (*phenylhydrazone*, silky, yellow needles, m. p. 130°); N-*cinnamoyl* derivative, silky, white prisms, m. p. 80—81° (*phenylhydrazone*, orange-red crystals, m. p. 148—149°); N-*ethoxalyl* derivative, needles, m. p. 100°; N-*carbethoxy*-derivative, CHAc⁚CMe·NH·CO_2Et, long, silky needles, m. p. 57°. The last-named compound reacts with liquid ammonia to form two *bases*, I, m. p. 206° (decomp.), and II, m. p. 72—74°:

$$\begin{array}{l} NH_2\cdot CMe(OH)\cdot CMe\cdot NH_2 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad NH\cdot CO\cdot NH_2 \end{array} \qquad CH_2\begin{cases} CMe{=}N{-}CO \\ \qquad\qquad\qquad | \\ CMe(NH_2)\cdot NH \end{cases}\cdot$$

(I.) (II.)

The clue to the constitution of these bases is furnished by the fact that they give the known bromine derivative of acetylacetonecarbamide [4:6-dimethyldihydropyrimid-2-one] on treatment with bromine water, whilst base II changes into this carbamide on heating, with or without alcohol (compare Evans, A., 1894, i, 111).

Phenyl β-ethoxalylamino-Δ^α-propenyl ketone,

COPh·CH⁚CMe·NH·CO·CO_2Et,

silky needles, m. p. 88—89°, is formed in a similar manner from benzoylacetonamine.

Acetylacetonamine also reacts with benzenediazonium chloride to form the *benzeneazo*-compound (*β-amino-α-benzeneazo-Δ^α-propenyl methyl ketone*), NPh⁚N·CAc⁚CMe·NH_2, slender, yellow spikes, m. p. 125°, which changes on keeping into benzeneazoacetylacetone, m. p. 90°, and yields the *phenylhydrazone* of this ketone, $C_{17}H_{18}ON_4$, as a mass of yellow needles, m. p. 185° (decomp.), when boiled with alcoholic phenylhydrazine, or 4-benzeneazo-1-phenyl-3:5-dimethylpyrazole, m. p. 62°, if heated with phenylhydrazine alone. J. C. W.

Allylbetaine and Allylhomocholine. J. von Braun and E. Müller (*Ber.*, 1917, **50**, 290—293).—The remarkable discovery that *N*-allylnorcodeine is physiologically antagonistic to morphine (A., 1916, i, 665) has induced the authors to investigate the influence of the introduction of an allyl group on the activity of other substances. In most cases, no such modification has been observed, but it is found that betaine and homocholine form N-allyl derivatives which are directly antagonistic to the parent bases, at any rate in their action on the poikilothermic heart.

Dimethyl-γ-hydroxypropylamine (*ibid.*, 631) combines with allyl iodide to form the quaternary *allyliodide*, m. p. 57—58°, from which the chloride can be made in the usual way. *Dimethyl-γ-hydroxypropylallylammonium chloride* (*allylhomocholine chloride*), OH·C_3H_6·NMe_2(C_3H_5)·Cl, is a viscous oil, which yields a *platinichloride*, m. p. 182°.

Methyl dimethylaminoacetate (Willstätter, A., 1902, i, 267) also forms an *allyliodide*, m. p. 83°, and this may be converted into N-*allylbetaine*, $C_3H_5\cdot NMe_2{<}^{CH_2}_{O}{>}CO$, m. p. 66°, by shaking with

silver oxide and silver chloride. The base is very hygroscopic, and yields a yellowish-red *platinichloride*, m. p. 174—175°, and a soluble *aurichloride*, yellow leaflets, m. p. 146°.

The following compounds were prepared by the usual methods, but are only briefly described, as they have no unexpected properties: 1-*Allylpyrrolidine*, volatile in steam or ether vapour; *platinichloride*, m. p. 205°, and *aurichloride*, m. p. 97—98°, both readily soluble in water. 1-*Allylthalline*, pale yellow, b. p. 176°/12 mm. 1-*Allyltheobromine*, colourless crystals, m. p. 147°. N-*Allylstrychnine*, from strychnine allyliodide by the action of silver sulphate, and then barium hydroxide. *Allyl sulphate*, from silver sulphate and allyl iodide; an unpleasant-smelling liquid which explodes on heating. J. C. W.

Imino-esters. II. Mechanism of the Formation of Amidines. ANGELO KNORR (*Ber.*, 1917, **50**, 229—236. Compare A., 1916, i, 797).—The formation of amidines by the action of ammonia on the hydrochlorides of imino-esters was explained by Pinner on the basis of the following equations: $RO{\cdot}CR'{:}NH,HCl + NH_3 = RO{\cdot}CR'{:}NH + NH_4Cl$; $RO{\cdot}CR'{:}NH + NH_3 = NH_2{\cdot}CR'{:}NH + R{\cdot}OH$; $NH_2{\cdot}CR'{:}NH + NH_4Cl = NH_2{\cdot}CR'{:}NH,HCl + NH_3$. Pinner knew, however, that ammonia had no action on free *iso*butyl iminobenzoate, and Stieglitz and his pupils have shown that this is the general rule in the case of esters of the type $NH_2{\cdot}C(OR){:}NH$, that is, the *iso*carbamides, assuming there to be, in consequence, a difference in constitution between these and the ordinary imino-esters (A., 1899, i, 359, 594). It is now found, also, that ammonia has no action on ethyl iminomethylthiolformate, $OEt{\cdot}C(SMe){:}NH$, although it reacts vigorously with the hydrochloride, the free ester, and later on guanidine hydrochloride, methyl mercaptan, and ethyl alcohol being formed. It is shown conclusively that it is ammonium chloride which reacts with the free esters to form amidine hydrochlorides, thus:

$$OR{\cdot}CR'{:}NH + NH_4Cl = NH_2{\cdot}CR'{:}NH,HCl + R{\cdot}OH.$$

Ethyl iminoacetate and iminobenzoate, for example, react quite readily with ammonium chloride, alone or diluted with alcohol or ether, whilst the above thio-ester (A., 1916, i, 797) reacts best in alcoholic solution. Ethyl*iso*carbamide also reacts easily to form guanidine hydrochloride, but phenylethyl*iso*carbamide,

$$NHPh{\cdot}C(OEt){:}NH,$$

is not affected by ammonium chloride. J. C. W.

The Simplest Organo-metallic Alkali Compounds. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, **50**, 262—274).—Organo-sodium and -lithium compounds have been obtained in a fairly pure state by the action of sodium on the corresponding organo-mercury compounds in light petroleum or benzene. The apparatus used was that designed for the preparation of metal ketyls (A., 1913, i, 1205), and the manipulation is fully described.

Sodium methyl, sodium ethyl, sodium n-*propyl, sodium octyl*, and *sodium phenyl* are colourless, amorphous substances, insoluble in indifferent media, which decompose without melting when heated. They inflame with violence when brought into the air, but the activity of this oxidation falls with increasing molecular weight. *Sodium benzyl*, CH_2PhNa, forms garnet-red crystals, and its ethereal solution will conduct the electric current, showing that the metallic atom is linked by a carbonium valence. It inflames in the air, yields much stilbene if the oxidation is slow, and reacts with carbon dioxide to form sodium phenylacetate.

The most convenient lithium compound to make by the above reaction is *lithium ethyl*. This crystallises from warm benzene in stout, hexagonal, limpid tablets, m. p. 95°. *Lithium methyl* and *lithium phenyl* are best prepared by mixing solutions of lithium ethyl and the mercury compounds, when they separate as white, microcrystalline precipitates, as, for example, according to the equation $2LiEt + HgMe_2 = 2LiMe + HgEt_2$. The lithium compounds inflame in the air; lithium methyl presents a fine spectacle, the flame being brilliant red accompanied by a shower of yellow sparks.

J. C. W.

Resistance of the Alkyl Groups attached to a Lead Atom to the Disruptive Action of Halogens. Preparation of Mixed Lead Alkyls containing Three or Four different Radicles. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 202—211. Compare A., 1916, i, 684, 800).—It has been found that when lead tetra-alkyls are treated with halogens at −75°, one alkyl group is removed, whilst at −20° a further group is lost. From the lead trialkyl haloid or lead dialkyl dihaloid so obtained, other alkyl groups can be reintroduced by the Grignard action, numerous examples having already been given. It is now stated that in all cases in which the alkyl groups are in primary attachment to the lead atom, it is the lightest group which is removed by the halogen. Working out this discovery to its logical conclusion, it has thus become possible to prepare lead tetra-alkyls with three or four different groups. As each of these can be obtained in different ways, but never as *cis-trans*-isomerides, the conclusion is drawn that the four valencies of lead are equivalent and probably arranged like those of carbon. Optical isomerism may be possible.

With the exception of the mixed lead trialkyl haloids, which do not crystallise, the compounds can all be obtained in a high degree of purity. The yields throughout are excellent. The following examples are given.

Lead dimethylethylpropyl, $PbMe_2EtPr^{\alpha}$. b. p. 65°/15 mm., D_4^{23} 1·6943, $n_D^{21\cdot8}$ 1·5110, $n_F - n_C$ 0·01687; *lead dimethylethylisobutyl*, b. p. 74°/13 mm., $D_4^{20\cdot7}$ 1·6234, n_H 1·50327, n_D 1·50783, $n_{H\beta}$ 1·51982, $n_{H\gamma}$ 1·53010, all at 20·7°; *lead methyldiethylpropyl*, b. p. 80·8°/15 mm., $D_4^{22\cdot1}$ 1·6403, $n_{H\alpha}$ 1·50925, n_D 1·51412, $n_{H\beta}$ 1·52638, $n_{H\gamma}$ 1·53710, at 22·1°; *lead dimethylethylisoamyl*, b. p. 92°/14 mm., $D_4^{21\cdot7}$ 1·5579, $n_{H\alpha}$ 1·50079, n_D 1·50524, $n_{H\beta}$ 1·51662, $n_{H\gamma}$ 1·52647, at 21·7°; *lead methyldiethyliso-*

butyl, b. p. 87°/13 mm., D_4^{20} 1·5812, $n_D^{19·5}$ 1·5120, $n_F - n_C$ 0·01664; *lead methyldiethyl*iso*amyl*, b. p. 106°/15·5 mm., $D_4^{20·8}$ 1·5225, $n_{H\alpha}$ 1·50336, n_D 1·50783, $n_{H\beta}$ 1·51921, $n_{H\gamma}$ 1·52934, at 20·8°; *lead dimethylpropyl*iso*amyl*, b. p. 105°/15 mm., D_4^{22} 1·5028, $n_{H\alpha}$ 1·49773, n_D 1·50201, $n_{H\beta}$ 1·51313, $n_{H\gamma}$ 1·52251, at 22°; *lead diethylpropyl*-n-*butyl*, b. p. 116°/vac., D_4^{23} 1·4789, $n_D^{21·4}$ 1·5100, $n_F - n_C$ 0·01547 (prepared from *lead triethyl*-n-*butyl*, b. p. 108°/13 mm., $D_4^{20·8}$ 1·5285, $n_D^{20·8}$ 1·5120, $n_F - n_C$ 0·01639); *lead diethylpropyl*iso*butyl*, b. p. 110°/13 mm., D_4^{20} 1·4890, $n_{H\alpha}$ 1·50751, n_D 1·51195, $n_{H\beta}$ 1·52353, $n_{H\gamma}$ 1·53359, at 20°; *lead diethylpropyl*iso*amyl*, b. p. 127·5°/15 mm., $D_4^{22·1}$ 1·4392, $n_{H\alpha}$ 1·50217, n_D 1·50655, $n_{H\beta}$ 1·51758, $n_{H\gamma}$ 1·52721, at 22·1°; *lead diethyl*iso*butyl*iso*amyl*, b. p. 131°/14 mm., $D_4^{21·5}$ 1·3980, $n_D^{19·3}$ 1·5053; *lead ethylpropyldi*iso*amyl*, b. p. 145·5°/13 mm., D_4^{20} 1·3552, $n_D^{18·8}$ 1·5039, $n_F - n_C$ 0·01524.

Lead methylethyl-n-*propyl*-n-*butyl* has b. p. 103°/13 mm., $D_4^{23·5}$ 1·5068, $n_D^{22·4}$ 1·5072, $n_F - n_C$ 0·01607; *lead methylethyl*-n-*propyl*iso*amyl* has b. p. 115°/15 mm., D_4^{21} 1·4792, $n_{H\alpha}$ 1·50189, n_D 1·50636, $n_{H\beta}$ 1·51747, $n_{H\gamma}$ 1·52720, at 21°; *lead ethyl*-n-*propyl*-n-*butyl*iso*amyl*, has b. p. 144°/14 mm., $D_4^{23·3}$ 1·3699, $n_D^{21·5}$ 1·5028, $n_F - n_C$ 0·01473.

The mixed lead dialkyl dihaloids are stable, crystalline salts. *Lead methylethyl dichloride*, $PbMeEtCl_2$, crystallises in filamentous needles, forms an additive compound with pyridine (very large needles), and gives precipitates of the white sulphide (soluble in hydrochloric acid or ammonium sulphide), the canary-yellow iodide, and the yellow chromate (soluble in acetic acid) when the appropriate reagents are added to its aqueous solution. *Lead ethyl*iso*amyl dichloride* forms pearly leaflets; *lead propyl*iso*amyl dichloride* crystallises in satiny leaflets; *lead ethyl*iso*butyl dibromide* separates in whetstone forms; *lead* n-*propyl*iso*butyl dibromide* forms bundles of satiny needles. J. C. W.

Organo-lead Compounds. VI. Lead Tetra*iso*amyl, Lead Tetra-*iso*butyl, Lead Tetra-*n*-propyl, and their Derivatives. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 278—285. Compare, especially, A., 1916, i, 684, 800).—Some more compounds of the types PbR_4, $PbR_3Hal.$, $PbR_2Hal._2$, and PbR_3R' are described.

*Lead tetra*iso*amyl* decomposes on heating, even in a high vacuum, but may be purified by distillation in a current of steam. It is an almost odourless, colourless oil; $D_4^{20·5}$ 1·2332, $n_{H\alpha}$ 1·49075, n_D 1·49457, $n_{H\beta}$ 1·50404, $n_{H\gamma}$ 1·51232, at 20·5°. *Lead tri*iso*amyl bromide* crystallises in long, snow-white needles, m. p. 132—133°. *Lead di*iso*amyl dichloride* forms white leaflets, decomp. 108°, and the *dibromide* pale yellow flakes. *Lead methyltri*iso*amyl* has D_4^{22} 1·3134, $n_{H\alpha}$ 1·49226, n_D 1·49618, $n_{H\beta}$ 1·50612, $n_{H\gamma}$ 1·51477, at 22°; *lead ethyl tri*iso*amyl* has $D_4^{19·6}$ 1·2922, $n_{H\alpha}$ 1·49425, n_D 1·49825, $n_{H\beta}$ 1·50818, $n_{H\gamma}$ 1·51669, at 19·6; *lead* n-*propyltri*iso*amyl* has D_4^{22} 1·2737, $n_{H\alpha}$ 1·49324, n_D 1·49703, $n_{H\beta}$ 1·50696, $n_{H\gamma}$ 1·51542, at 22°; *lead* iso*butyltri*iso*amyl* has $D_4^{19·5}$ 1·2522, $n_{H\alpha}$ 1·49242, n_D 1·49618, $n_{H\beta}$ 1·50597, $n_{H\gamma}$ 1·51428, at 19·5°. These oils are all purified by distillation in

steam, followed by warming under reduced pressure in an atmosphere of hydrogen.

*Lead tetra*iso*butyl* crystallises in white leaflets, m. p. $-23°$ (corr.), $D_4^{20\cdot2}$ 1·3240, n_{H_α} 1·50004, n_D 1·50416, n_{H_β} 1·51461, n_{H_γ} 1·52375, at 20·2°. *Lead tri*iso*butyl chloride* forms long needles, m. p. 122° (decomp.), the *bromide* crystallises in very long, glistening needles, m. p. 107—108°, and the *iodide* forms unstable, yellow leaflets. *Lead di*iso*butyl dichloride* crystallises in white leaflets, decomp. above 100°, and the *dibromide* in pale yellow leaflets, decomp. 102—103°. *Lead di*iso*butyl chlorobromide*, $Pb(C_4H_9)_2ClBr$, prepared by the action of bromine on lead tri*iso*butyl chloride, crystallises in hard, compact, very long, flat, glistening spikes, decomp. 110°. *Lead methyltri*iso*butyl* has b. p. 121°/12 mm. (slight decomp.), $D_4^{19\cdot6}$ 1·3977, n_{H_α} 1·49883, n_D 1·50321, n_{H_β} 1·51397, n_{H_γ} 1·52324, at 19·6°; *lead ethyltri*iso*butyl* has $D_4^{22\cdot1}$ 1·3758, n_{H_α} 1·50134, n_D 1·50552, n_{H_β} 1·51636, n_{H_γ} 1·52573, at 22·1°; *lead* n-*propyltri*iso*butyl* has $D_4^{19\cdot6}$ 1·3505, n_{H_α} 1·50148, n_D 1·50561, n_{H_β} 1·51631, n_{H_γ} 1·52554, at 19·6°; *lead tri*iso*butyl*iso*amyl* has $D_4^{20\cdot6}$ 1·2976, n_{H_α} 1·49696, n_D 1·50097, n_{H_β} 1·51118, n_{H_γ} 1·51989, at 20·6°.

Lead methyltri-n-*propyl* has b. p. 106°/13 mm., $D_4^{22\cdot3}$ 1·5220, n_{H_α} 1·50456, n_D 1·50911, n_{H_β} 1·52059, n_{H_γ} 1·53058, at 22·3°; *lead ethyltri*-n-*propyl* has b. p. 118·2°/14 mm., $D_4^{21\cdot3}$ 1·4846, n_{H_α} 1·50703, n_D 1·51149, n_{H_β} 1·52290, n_{H_γ} 1·53299, at 21·3°; *lead tri*-n-*propyl*iso*butyl* has $D_4^{22\cdot6}$ 1·4034, n_{H_α} 1·50235, n_D 1·50673, n_{H_β} 1·51766, n_{H_γ} 1·52716, at 22·6°; *lead tri*-n-*propyl*iso*amyl* has D_4^{21} 1·3810, n_{H_α} 1·50049, n_D 1·50465, n_{H_β} 1·51535, n_{H_γ} 1·52462, at 21°.

Lead n-*propyl*iso*butyl dichloride* crystallises in very stable, sparingly soluble, rounded leaflets, and *lead* iso*butyl*iso*amyl dibromide* forms elongated, transparent, pale yellow leaflets, decomp. 95°.

[All the densities recorded in this and the preceding paper are reduced to vacuum standard.] J. C. W.

Optical Activity of Low Temperature- and Generator-coal Tars. FRANZ FISCHER and W. GLUUD (*Ber.*, 1917, **50**, 111—115).—In a recent communication (A., 1916, i, 800), Pictet, Ramseyer, and Kaiser reported that they had obtained optically active substances from coal by extraction with benzene, but not by distillation in a vacuum. They concluded, therefore, that the coal had not experienced a temperature as high as 450° during its formation. In connexion with other work, however, the present authors have observed optical activity, beyond the limits of experimental error, with extracts of tars obtained from coals of the same origin (Saar and Lower Rhine) by low temperature (450—550°) and generator processes. The isolation of the most active fractions is described; they are insoluble in acids, alkalis, or liquid sulphur dioxide. J. C. W.

Preparation of *o*-Chlorotoluene. BADISCHE ANILIN- & SODA-FABRIK. (D.R.-P., 294638; from *J. Soc. Chem. Ind.*, 1917, **36**, 286). —Toluene-*p*-sulphonic acid or its chloride or amide is dissolved in

sulphuric acid, the solution treated with chlorine, and the sulphonic group removed from the resulting *o*-chlorotoluene-*p*-sulphonic acid, for example, by heating it in a current of steam.

H. W.

***o*-Vinylbenzyl Bromide and its Derivatives.** J. VON BRAUN (*Ber.*, 1917, **50**, 45—49).—A mixture of *o*-vinylbenzyl bromide and 1-cyanopiperidine was recently described as the product of the action of cyanogen bromide on 1-*o*-vinylbenzylpiperidine (this vol., i, 169). Attempts to isolate the former substance from the mixture have been unsuccessful, and therefore choice was made of *o*-vinylbenzyldimethylamine (Emde, A., 1912, i, 801) as a source, for this would yield as a second product a cyanoamine of much lower b. p. or one soluble in acids.

o-Vinylbenzyldimethylamine is best obtained by distilling dimethyltetrahydro*iso*quinolinium hydroxide under reduced pressure. It reacts vigorously with cyanogen bromide in ethereal solution, giving the desired bromide and cyanodimethylamine in the solution and a small deposit of a *quaternary bromide* compounded of the bromide and the original base,

$$(CH_2{:}CH\cdot C_6H_4\cdot CH_2)_2NMe_2Br,$$

m. p. 178—179°. The cyanodimethylamine is extracted from the ethereal solution by means of a dilute acid, leaving *o-vinylbenzyl bromide* as a colourless, mobile, heavy oil, b. p. 119—120°/17 mm. As a benzyl bromide derivative, it has the characteristic irritating odour, and reacts readily with water, alcohol, amines, sodiomalonic esters, etc., giving products which will be described later. As a derivative of styrene, it polymerises even in the dark, and combines directly with hydrogen (Paal's method), halogens, or halogen hydrides. o-*Ethylbenzyl bromide* has b. p. 120—121°/23 mm. o-*αβ-Dibromoethylbenzyl bromide* crystallises in stout prisms, m. p. 46°. o-*α-Bromoethylbenzyl bromide*, obtained by shaking the unsaturated bromide with fuming hydrobromic acid, is a snow-white, crystalline mass, m. p. 36—37°, which reacts with dimethylamine according to the equation

$$C_6H_4{<}{\begin{matrix}CHBrMe\\CH_2Br\end{matrix}} + 2NHMe_2 =$$

$$C_6H_4{<}{\begin{matrix}CHMe\\CH_2\end{matrix}}{>}NMe_2Br + NHMe_2,HBr.$$

The *quaternary bromide*, silvery leaflets, m. p. 216°, is precipitated from the aqueous solution of the mixture by the addition of alkali hydroxide. The corresponding *platinichloride*,

$$C_{22}H_{30}N_2,H_2PtCl_6,2H_2O,$$

crystallises in leaflets, m. p. 201°.

o-Ethylbenzyl bromide can also be obtained from 1-o-*ethylbenzylpiperidine*. This base is prepared by reducing the corresponding vinyl compound (*loc. cit.*); it has b. p. 147°/18 mm., and forms a *hydrochloride*, leaflets, m. p. 212—213°, an *aurichloride*, m. p. 158°, a *picrate*, and a *methiodide*, m. p. 145—146°. The base reacts with cyanogen bromide to give a mixture of 1-cyano-

piperidine and *o*-ethylbenzyl bromide, and the latter can be isolated by boiling the oil with hydrobromic acid until the former is hydrolysed and dissolved. J. C. W.

The Indene Series. IV. J. von Braun, E. Danziger, and Z. Koehler (*Ber.*, 1917, **50**, 56—64. Compare this vol., i, 130).—For comparison with 2-amino-2-methylhydrindene, (I), the authors have synthesised the isomerides, (II, III, and IV), and have attempted to prepare the nearly related aromatic–aliphatic base, (V):

$$C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CMe\cdot NH_2 \quad \text{(I.)} \qquad C_6H_4<\begin{matrix}CH_2 & \\ CH\text{—} & \end{matrix}\begin{matrix}CH_2 \\ \text{—}CH_2\cdot NH_2\end{matrix} \quad \text{(II.)}$$

$$C_6H_4<\begin{matrix}\text{—}CH_2\text{—}\\CHMe\end{matrix}>CH\cdot NH_2 \quad \text{(III.)} \qquad C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CH_2\cdot NH_2 \quad \text{(IV.)}$$

$$CH_2Ph\cdot CMe_2\cdot NH_2. \quad \text{(V.)}$$

The corresponding alcohols are also described.

1-*Hydrindylmethylamine*, (II).—α-Hydrindone is condensed with ethyl bromoacetate in the presence of zinc to form *ethyl 1-hydrindylideneacetate*, as a viscous oil, b. p. 166—168°/10 mm. This ester yields a resin if warmed with sodium hydroxide, and 1-methylindene if hydrolysed by dilute sulphuric acid. If it is purified by shaking with sodium hydroxide and then fractionating, it yields on reduction by the Paal-Skita method only 1-*methylhydrindene*, b. p. 182—183°, D_4^{16} 0·9661, n_D 1·53938, but if it is first fractionated, treated with alkali to remove a minute trace of bromine, redistilled, and then reduced, it gives the normal product, *ethyl 1-hydrindylacetate*, as a pleasant-smelling, limpid oil, b. p. 149—150°/12 mm. The saturated ester can be readily hydrolysed to 1-*hydrindylacetic acid*, glistening leaflets, m. p. 60—61°, and this converted into the *chloride*, b. p. 146°/11 mm., which condenses readily with aromatic hydrocarbons, etc., but does not undergo internal condensation under the influence of aluminium chloride. The *amide*, m. p. 90°, is prepared from the chloride, and the *hydrazide*, matted needles, m. p. 113° (*hydrochloride*, m. p. 208°), by the action of hydrazine hydrate on the ester. Finally, 1-*hydrindylmethylamine*, (II), is obtained by the Hofmann reaction, or, better, from the hydrazide, through the urethane, as a colourless liquid, b. p. 125—126°/13 mm., with a not very intense odour. It forms a *hydrochloride*, m. p. 212—214°, a *platinichloride*, decomp. 235°, and a *picrate*, m. p. 176—177°.

β-1-*Hydrindylethyl alcohol*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CH\cdot CH_2\cdot CH_2\cdot OH\end{matrix}$, b. p. 150—152°/11 mm., is prepared by the reduction of ethyl

1-hydrindylacetate with sodium and alcohol. Unlike the open aromatic–aliphatic alcohols, it is an almost odourless, syrupy liquid, and the corresponding *β-1-hydrindylethyl chloride*, b. p. 132—134°/14 mm., has a much fainter odour than the homologues of benzyl chloride.

2-Amino-1-methylhydrindene, (III).—1-Methylhydrindene-2-carboxylic acid is obtained from ethyl benzylacetoacetate (Roser, A., 1888, 1303). The *chloride*, b. p. 150°/20 mm., is converted into the *amide*, m. p. 130°, and this into *2-amino-1-methylhydrindene*, b. p. 108—110°/11 mm., by Hofmann's method. The base forms a *hydrochloride*, m. p. 202°, a *picrate*, m. p. 239°, and a *benzoyl* derivative, m. p. 137°.

Ethyl 1-methylhydrindene-2-carboxylate, b. p. 150—151°/11 mm., may be reduced to *1-methyl-2-hydrindylmethyl alcohol*,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2—}{CHMe}}{>}CH{\cdot}CH_2{\cdot}OH,$$

an odourless, viscous oil, b. p. 148—150°/11 mm., the corresponding *chloride* having b. p. 135—138°/11 mm.

2-Hydrindylmethylamine (IV).—This base was already known (Kenner, T., 1914, **105**, 2696). It forms a *picrate*, m. p. 180—182°, a *benzoyl* derivative, m. p. 120—121°, and a *salicylidene* compound, m. p. 66°.

β-Chloro*iso*amylbenzene (Klages, A., 1904, i, 497) is practically indifferent towards ammonia or amines at the ordinary temperature, and under drastic treatment yields ββ-dimethylstyrene (*ibid.*).

J. C. W.

The State of Saturation of the Unsaturated Linking. I. H. Ley (*Ber.*, 1917, **50**, 243—250).—It is a well-known fact that the additive capacity of a compound with an ethylenic linking is greatly influenced by the nature of the atoms or groups attached to the doubly linked carbon atoms. For example, styrene and stilbene readily unite with bromine, but tetraphenylethylene does not. It is common to offer the suggestion that such a difference as this is due to steric hindrance, but the author prefers to account for the facts by assuming changes to take place in the degree of saturation of the ethylene linking. He proposes to develop his arguments on the basis of electroatomic theories, the usual valency ideas being obviously insufficient.

The absorption spectra reveal also, even in cases where arguments on steric lines cannot hold, that the degree of saturation can be modified considerably by apparently small changes. The spectrum of stilbene, for example, is distinctly modified by the presence of a methyl group (α-methylstilbene) in the direction of that of the fully saturated, closely related compound, dibenzyl. The spectra of cinnamic acid and α- and β-methylcinnamic acids show similar relationships. Phenylstilbene, α-phenylcinnamic acid, and α-methylstyrene are mentioned in the same connexion, but exact quantitative comparisons will apparently be made later on, and a full discussion raised then.

The extinction coefficients of comparable solutions of the addi-

tive compounds of stilbene and α-methyl- and α-phenyl-stilbene with *s*-trinitrobenzene have also been roughly determined. In agreement with Werner's rule, that such molecular compounds possess deeper colours the more unsaturated the hydrocarbon is (A., 1910, i, 20), the conclusion must be drawn that stilbene is the most unsaturated of the three.

This effect of the introduction of an alkyl radicle is quite the opposite when the group enters a cyclic system, for it is well known that in respect of absorption and formation of molecular compounds, toluene and hexamethylbenzene behave as more unsaturated compounds than benzene (compare Werner, *ibid.*, and Pfeiffer, A., 1914, i, 551). J. C. W.

The Bucherer Reaction. HARTWIG FRANZEN and HUBERT KEMPF (*Ber.*, 1917, **50**, 101—104).—The Bucherer reaction, whereby amines can be converted into phenols through the action of sulphites (A., 1902, i, 718; 1903, i, 627; 1904, i, 309; 1905, i, 48, 585; 1907, i, 509; 1908, i, 455; 1909, i, 521, 787; 1910, i, 144), is fundamentally a process of hydrolysis, according to the equation $ArNH_2 + H_2O = ArOH + NH_3$. Regarded in this light, it is remarkable that a reaction which is notoriously difficult of achievement by the strong mineral acids should be brought about by sulphurous acid. The authors have therefore made some comparative tests on the hydrolysis of the naphthylamines and naphthionic acid by hydrochloric, sulphuric, phosphoric, phosphorous, boric, arsenious, hypophosphorous, and sulphurous acids, using as the criterion the amount of ammonia developed after one, two, three, or four days. As only the last two acids produce any notable effects, the others being about equally indifferent, the conclusion is drawn that the hydrolysis of aromatic amines is governed by the degree of unsaturation rather than by the strength of the acid. J. C. W.

Benzyltetramethylammonium. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, **50**, 274—275).—When a solution of sodium benzyl (this vol., i, 256) in cold ether is shaken with dried tetramethylammonium chloride in an atmosphere of nitrogen, *benzyltetramethylammonium*, $CH_2Ph{\cdot}NMe_4$, is formed, as a brilliant red, granular powder (compare the analogous preparation of triphenylmethyltetramethylammonium, A., 1916, i, 385). This is either insoluble in or decomposed by ordinary solvents, even pyridine, and is hydrolysed by water to toluene and tetramethylammonium hydroxide. J. C. W.

Ammonium Compounds of a New Type. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1917, **50**, 276—278).—If an ethereal solution of potassiodi-*p*-tolylamine (A., 1914, i, 823) is shaken with dried tetramethylammonium chloride in an atmosphere of nitrogen, *di*-p-*tolylaminotetramethylammonium*, $Me_4N{\cdot}N(C_7H_7)_2$, is formed. This crystallises from pyridine in greenish-yellow leaflets, which soon become brown in the air, and is hydrolysed by water to ditolylamine and tetramethylammonium hydroxide. Although the two nitrogen atoms are linked together, the sub-

stance is therefore a salt, which is of considerable interest in connexion with the function and distribution of the fifth valence of nitrogen. The pyridine solution is also an electrolyte, the equivalent conductivity being = 5·72.

Diphenylaminotetramethylammonium is a very similar substance, crystallising in greenish-yellow needles. J. C. W.

Phenol Bases. III. J. VON BRAUN and E. DANZIGER (*Ber.*, 1917, **50**, 286—289).—The introduction of a phenol group in the para-position in β-phenylethylamine and homologous bases is known to have the effect of increasing their physiological activity, but such seems not to be the case with 2-amino-2-methylhydrindene (this vol., i, 130). The new phenolic base has been prepared through the nitro-, amino-, and hydroxy-derivatives of 2-acetylamino-2-methylhydrindene.

5-*Nitro-2-acetylamino-2-methylhydrindene*, the sole product of the action of fuming nitric acid at 0°, has m. p. 144—145°; 5-*amino-2-acetylamino-2-methylhydrindene* has m. p. 153—154°, and forms an unstable, white hydrochloride, a *picrate*, m. p. 215°, and a *benzoyl* derivative, m. p. 206°; 2-*acetylamino-5-hydroxy-2-methylhydrindene* has m. p. 112°; and 2-*amino-5-hydroxy-2-methylhydrindene*, $OH\cdot C_6H_3{<}^{CH_2}_{CH_2}{>}CMe\cdot NH_2$, is a very pale pink, microcrystalline powder, m. p. 154°, which yields a very soluble hydrochloride, a red *platinichloride*, m. p. 229°, a *picrate*, m. p. 240°, and a *dibenzoyl* derivative, m. p. 180°.

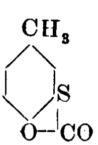
5-*Nitro-2-amino-2-methylhydrindene* is an oily base, which forms a *hydrochloride*, and a *picrate*, m. p. 220°. J. C. W.

3-Thiol-*p*-cresol. TH. ZINCKE and K. ARNOLD (*Ber.*, 1917, **50**, 116—126).—3-Thiol-*p*-cresol has been known hitherto only in the form of bromine derivatives (A., 1911, i, 287). It has now been isolated, and a number of related compounds prepared.

An alkaline solution of potassium *p*-cresol-3-sulphonate (*ibid.*) is shaken with ethyl chloroformate, and thus converted into *potassium 4-ethylcarbonatotoluene-3-sulphonate*,

$$CO_2Et\cdot O\cdot C_6H_3Me\cdot SO_3K,$$

which crystallises in long needles. The corresponding *sulphonyl chloride*, large, stout crystals, m. p. 59°, may be converted into the *sulphonanilide*, m. p. 126°, or reduced by means of zinc dust and alcohol to the mercaptan. Only a trace of the mercaptan can actually be isolated, as it is very unstable. The main products are the oxidation product, 4-*ethylcarbonatotolyl 3-disulphide*, $(CO_2Et\cdot O\cdot C_6H_3Me)_2S_2$, stout crystals, m. p. 73°, and the *carbonate* (annexed formula), long spikes, m. p. 83°. This carbonate may be hydrolysed by aqueous-alcoholic sodium hydroxide to 3-*thiol*-p-*cresol*, $OH\cdot C_6H_3Me\cdot SH$, which is a limpid liquid, b. p. 110—112°/18 mm., with a peculiar, not unpleasant odour. The *dibenzoate* forms colourless needles, m. p. 86°.



A number of ethers of 3-thiol-*p*-cresol, and their

bromination and oxidation, are described. Methyl iodide reacts in the presence of sodium methoxide to form 3-*methylthiol*-p-*cresol*, b. p. 118—120°/18 mm., which yields 2:5-dibromo-3-methylthiol-*p*-cresol dibromide (*ibid.*) when treated with bromine. Methyl sulphate gives the dimethyl ether, 4-*methoxy*-3-*methylthioltoluene*, b. p. 145—150°/39 mm., which reacts with bromine to form 5-*bromo*-4-*methoxy*-3-*methylthioltoluene dibromide*,

$OMe{\cdot}C_6H_2MeBr{\cdot}SMeBr_2$,

in dark reddish-brown needles, and this is readily converted into 5-*bromo*-4-*methoxy*-3-*methylthioltoluene*, colourless needles, m. p. 63—64°, when shaken with sodium hydrogen sulphite. Benzyl chloride reacts in the presence of alkali to form the two benzyl ethers. 4-*Benzyloxytoluene*-3-*benzylthiol*,

$CH_2Ph{\cdot}O{\cdot}C_6H_3Me{\cdot}S{\cdot}CH_2Ph$,

forms colourless needles, m. p. 85°, and may be oxidised in glacial acetic acid solution by means of perhydrol to the *sulphoxide*, slender needles, m. p. 106—107°, and then to the *sulphone*, long, white needles, m. p. 138°. 3-*Benzylthiol*-p-*cresol*, b. p. 190—192°/21 mm., yields an *acetate*, slender needles, m. p. 63°, and may also be oxidised to a *sulphoxide*, m. p. 84°, and a *sulphone*,

$OH{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}CH_2Ph$,

stout prisms, m. p. 146°, the *acetate* of which forms colourless leaflets, m. p. 128°.

If 3-thiol-*p*-cresol or either of its benzyl ethers is treated with bromine, 2:4-*dibromo*-p-*cresol* 3-*disulphide*, $(OH{\cdot}C_6HMeBr_2)_2S_2$, is formed, in stout, pale yellow crystals, m. p. 174—175°; the *acetyl* derivative has m. p. 163°.

When a mixture of ethylcarbonato-*p*-cresol-3-sulphonyl chloride and sodium hydrogen carbonate is added to a solution of sodium sulphite, 4-*ethylcarbonatotoluene*-3-*sulphinic acid*,

$CO_2Et{\cdot}O{\cdot}C_6H_3Me{\cdot}SO_2H$,

is formed, in stout, monoclinic prisms, m. p. 102°. This yields a *methyl* ester (from the silver salt), glistening prisms, m. p. 121°, and may be hydrolysed to p-*cresol*-3-*sulphinic acid*, a very hygroscopic mass which gives a deep blue colour in concentrated sulphuric acid. *Methyl* 4-*methoxytoluene*-3-*sulphinate*,

$OMe{\cdot}C_6H_3Me{\cdot}SO_2Me$,

long needles, m. p. 88°, is obtained by treating this acid with methyl sulphate or by oxidising the above 4-methoxy-3-methylthioltoluene. J. C. W.

***p*-Phenetyltellurium Compounds.** KARL LEDERER (*Ber.*, 1917, **50**, 238—243).—The author suggested that compounds which Rohrbaech described as di-*p*-anisyl and di-*p*-phenetyl tellurides were really methylene compounds (A., 1916, i, 208) and has already given an account of the true di-*p*-anisyl telluride (*ibid.*, 647). *Di*-p-*phenetyl telluride*, $Te(C_6H_4{\cdot}OEt)_2$, is prepared by the action of tellurium dibromide on magnesium *p*-phenetyl bromide. It crystallises in matted needles, m. p. 63°, b. p. 235—240°/18 mm., and forms the following *additive* compounds with the mercuric haloids; *chloride*, elongated, quadrilateral platelets, m. p. 150—151°;

bromide, iridescent scales, m. p. 155—156°; *iodide*, a yellow powder, m. p. 123—124°. The *di*-p-*phenetyltelluronium* compounds described are the *dichloride*, $(C_6H_4{\cdot}OEt)_2TeCl_2$, needles, m. p. 125°; *dibromide*, four-sided columns from ether or scales from alcohol, m. p. 116—117°; *di-iodide*, ruby-red crystals, m. p. 134—135°; *oxide*, m. p. 135—148° (indefinite); and *methiodide*, m. p. 69°.

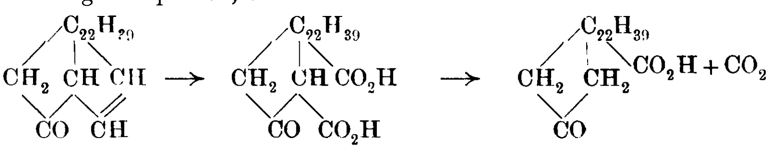
Phenyl-*p*-tolyltelluronium oxide (*ibid.*, 810) has m. p. 154—155°.

J. C. W.

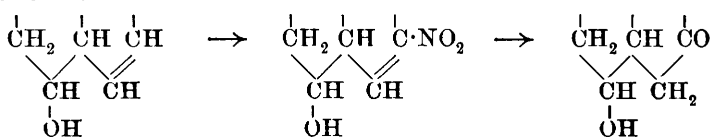
Cholesterol. XXV. A. Windaus (*Ber.*, 1917, **50**, 133—137).—When the ketone corresponding with cholesterol, namely, cholestenone, is oxidised with potassium permanganate, a monobasic ketonic acid is formed (A., 1906, i, 579). This was originally supposed to have the formula $C_{26}H_{42}O_3$, and its production was taken as evidence of the existence of a vinyl group in cholesterol, thus:

$$CH_2{:}CH{\cdot}C_{23}H_{39}{<}\begin{matrix}CH_2\\|\\CO\end{matrix} \longrightarrow CO_2H{\cdot}C_{23}H_{39}{<}\begin{matrix}CH_2\\|\\CO\end{matrix} + CO_2 + H_2O.$$

It is now found, however, that the acid really has the formula $C_{26}H_{44}O_3$, which destroys the accepted view that cholesterol has an unsaturated group at the end of a chain. The ethylene linking can only be in a ring, in such a position that a β-ketonic dicarboxylic acid and then a ketonic monocarboxylic acid is formed when the ring is ruptured, thus:



Further evidence in support of this view is now recognised in the established fact that cholesterol can be nitrated and the nitro-compound reduced by means of zinc and acetic acid to a ketone-alcohol, cholestanonol (A., 1904, i, 49). This recalls the conversion of indene into nitroindene and then into β-hydrindone, and may be formulated thus:



Cholestanonol may be reduced by sodium and alcohol to *cholestandiol*, $C_{27}H_{46}O_2$, leaflets and prisms, m. p. 216°, which yields a *diformate*, long needles, m. p. 150°, and may be converted by means of phosphorus pentachloride into the corresponding *dichlorocholestane*, hexagonal leaflets, m. p. 128°. This forms β-cholestane when boiled with sodium and amyl alcohol, but this hydrocarbon can be obtained much more readily from cholestanonol derivatives

(cholestandione, oxycholestenone, *β*-cholestanone, etc.) by reduction with amalgamated zinc and hydrochloric acid (Clemmensen's method). J. C. W.

Transformation of α-Glycols. F. COMA Y ROCA (*Anal. Fis. Quim.*, 1917, **15**, 29—50).—An investigation of the influence of the methoxyl group on the transformation of *α*-glycols. *α-Phenyl-αβ-di-*p*-anisylethylene glycol*, prepared by the interaction of *p*-anisoin and magnesium phenyl bromide, forms colourless crystals, m. p. 163—168°. Sulphuric acid of 30% strength converts it into *phenyl-di-*p*-anisylacetaldehyde*, colourless crystals, m. p. 88—89°, which yields an *oxime*, m. p. 132—133°, and a *semicarbazone*, m. p. 186—187°, and is converted by alcoholic potash into *phenyldi-*p*-anisylmethane*, colourless crystals, m. p. 100—101°.

*γ-Phenyl-αβ-di-*p*-anisylpropylene glycol* is obtained from *p*-anisoin and magnesium benzyl chloride, and forms crystals, m. p. 152—153°. It is converted by 30% sulphuric acid into *β-phenyl-αα-di-*p*-anisylpropaldehyde*, colourless crystals, m. p. 71—72°, which yields an *oxime*, colourless crystals, m. p. 116—118°, and is transformed by alcoholic potash into *α-phenyl-ββ-di-*p*-anisylethane*, crystals, m. p. 89—90°.

*Di-*p*-anisylbenzylcarbinol*, m. p. 140—141°, is prepared by the action of magnesium benzyl chloride on di-*p*-anisyl ketone, and is converted by acetyl chloride into *α-phenyl-ββ-di-*p*-anisylethylene*, m. p. 61—62°, which is reduced by sodium and alcohol to phenyl-di-*p*-anisylethane.

Magnesium *iso*butyl bromide and amygdalic acid yield *α-phenyl-ββ-di*iso*butylethylene glycol*, m. p. 72—73°. With magnesium *iso*amyl bromide the product is *α-phenyl-ββ-di*iso*amylethylene glycol*, needles, m. p. 109—110°.

The interaction of *p*-anisole and magnesium phenyl bromide, expected to yield diphenyldi-*p*-anisylethylene glycol, formed a *substance*, m. p. 164—165°, and another *substance*, m. p. 174—175°, separable by fractional crystallisation.

The dehydration of glycols containing methoxyl produces aldehydes; that of other glycols yields ketones. A. J. W.

Spectrochemistry of Benzene Derivatives. Cinnamic Esters. Hydroxystyrenes and their Ethers. K. VON AUWERS (*Annalen*, 1917, **413**, 253—309).—In his researches to determine the influence of ring formation on the spectrochemical behaviour of organic compounds, the author has been led to compare definite groups of substances, for example, the esters of cinnamic acids with those of coumarilic acids and certain styrene derivatives with coumarones and coumaranones. The results of these comparisons will be given in a later paper, the purpose of the present communication being to ascertain how far the spectrochemical regularities which have been determined for the simpler aromatic compounds are applicable to compounds of partly different structure. In comparing different compounds the author, according to his usual custom, employs the specific exaltation, $E\Sigma$, as the typical and characteristic spectrochemical value.

Esters of Cinnamic Acids.—The methyl and ethyl esters of thirteen cinnamic acids containing methyl or ethyl groups as substituents have been examined. It is found that the substituents, as usual, influence the spectrochemical behaviour of the parent substance according to their position. Situated in the side-chain, they depress the exaltation of the optical constants, the ethyl group in many instances more so than the methyl. Particularly noticeable is the depressing influence of two such alkyl groups, the specific exaltations of ethyl cinnamate being lowered to one-third or one-fourth of their value in the $\alpha\beta$-dimethylcinnamate and $\alpha\beta p$-trimethylcinnamate. A methyl group in the para-position generally increases the exaltation; in the ortho-position it does not change the exaltation of the dispersion, but slightly depresses the exaltation of the specific rotation.

The influence of a methoxy-substituent in an alkyl cinnamate is not so simple as in the case of the benzene molecule. The variation of its influence on the exaltation with its position is different according as the cinnamate does or does not contain a methyl group in the α- or β-position, and the original must be consulted for details, and also for the variations of the exaltations of six pairs of stereoisomeric cinnamates and of various styrene derivatives.

The following new compounds are described: *Propyl coumarate*, $OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Pr$, clusters of colourless needles, m. p. 71—72°, prepared from the silver salt and propyl iodide in boiling ether. *Methyl* α-p-*dimethylcinnamate*, $C_6H_4Me{\cdot}CH{:}CMe{\cdot}CO_2Me$, prepared by condensing *p*-tolualdehyde and methyl propionate, is an oil, b. p. 151°/14 mm., $D_4^{18\cdot3}$ 1·0507, n_α 1·55635, n_D 1·56400, n_β 1·58432, and n_γ 1·60362 at 18·3°; the free *acid* forms colourless needles, m. p. 169—170°. *Methyl* 6-*methoxy*-α-3-*dimethylcinnamate*, $C_{13}H_{16}O_3$, prepared in a similar manner from 6-methoxy-*m*-tolualdehyde, is an oil, b. p. 168°/11 mm., $D_4^{14\cdot6}$ 1·0989, n_α 1·55727, n_D 1·56424, and n_β 1·58477 at 14·6°; the free *acid* forms stout prisms, m. p. 122°. 6-*Methoxy*-β-3-*dimethylcinnamic acid*, $C_{12}H_{14}O_3$, felted needles, m. p. 113—115°, prepared from the crude ester obtained from β-5-dimethyl-*o*-coumaric acid and methyl sulphate, yields a pure *methyl* ester, stout prisms, m. p. 36°, b. p. 163·2—164·4°/11 mm., $D_4^{12\cdot7}$ 1·0872, n_α 1·54083, n_D 1·54716, n_β 1·56290, and n_γ 1·57804 at 12·7°, n_D^{20} 1·5439. o-*Methoxystyryl methyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COMe$, large prisms, m. p. 48—50°, b. p. 180—182°/20 mm., is obtained from the *o*-hydroxy-compound, 2*N*-sodium hydroxide, and methyl sulphate; it has $D_4^{61\cdot4}$ 1·0534, n_α 1·57525, n_D 1·58591, n_β 1·61640 at 61·4°. β-*Acetoxy*-α-*methylstyrene*, $CPhMe{:}CH{\cdot}OAc$, prepared by boiling hydratropaldehyde with acetic anhydride and anhydrous sodium acetate, is an oil having $D_4^{15\cdot2}$ 1·0574, n_α 1·53680, n_D 1·54278, n_β 1·55801, and n_γ 1·57204 at 15·2°.

β-*Bromo*-β-o-*tolylpropionic acid*, $C_{10}H_{11}O_2Br$, stout prisms, m. p. 125—126°, obtained by treating *o*-methylcinnamic acid with hydrobromic acid (saturated at 0°) first in the cold and then at the ordinary temperature, is converted by warm sodium carbonate solution into an oil, the greater part of which polymerises on distil-

lation, but the portion which distils is o-*methylstyrene*, an oil with a sweet odour, b. p. 55·4°/12 mm., $D_4^{13·25}$ 0·9168, n_α 1·54219, n_D 1·54817, n_β 1·56499, and n_γ 1·58003 at 13·25°.

The reaction between magnesium methyl iodide and ethyl *m*-hydroxybenzoate in ether leads to the formation of m-*hydroxyphenyldimethylcarbinol*, $OH·CMe_2·C_6H_4·OH$, prisms, m. p. 105—106°, which develops a blue coloration with aqueous ferric chloride and is converted by prolonged boiling with acetic anhydride into the *acetate*, $C_{11}H_{12}O_2$, b. p. 124°/12 mm., of 3-*hydroxy-α-methylstyrene*, $OH·C_6H_4·CMe:CH_2$, b. p. 119°/11 mm., $D_4^{13·0}$ 1·0476, n_α 1·56721, n_D 1·57337, n_β 1·59064, and n_γ 1·60612 at 13·0°. The latter condenses with monochloroacetic acid in aqueous sodium hydroxide to form 3-iso*propenylphenoxyacetic acid*, $C_{11}H_{12}O_3$, flat needles, m. p. 98°. C. S.

Isomerism of Formylphenylacetic Esters. IV. Methyl Formylphenylacetate. WILHELM WISLICENUS [with KURT BÖRNER, PAUL KURTZ, and ERNST A. BILHUBER] (*Annalen*, 1916, **413**, 206—252. Compare A., 1912, i, 623; 1900, i, 9, 597).—In 1894, Bishop, Claisen, and Sinclair described methyl formylphenylacetate as a viscous oil, b. p. 135—136°/14 mm. The authors have now thoroughly examined it. The preparation of the *sodium* and *potassium* derivatives from methyl phenylacetate, methyl formate, and sodium or potassium in absolute ether is described. Other derivatives described are the normal *copper*, $(C_{10}H_9O_3)_2Cu$, green crystals, m. p. 194—196° (decomp.), basic *copper methoxide*, $(C_{10}H_9O_3)Cu·OMe$, decomp. 204°, *nickel* compound, pale green needles with $1\frac{1}{2}$MeOH, and *cobalt* compound, rose needles with $1\frac{1}{2}$MeOH.

By acidifying the sodium or potassium derivative, the ester is obtained as a viscous oil, b. p. 123—125°/12 mm., which usually sets to a crystalline mass. The authors find that two modifications, both of which are crystalline, exist; "mixed" modifications corresponding with the β- and Michael's modifications of the ethyl ester (*loc. cit.*) do not occur.

The α-modification is prepared (1) by acidifying the copper derivative, (2) by the gradual addition of an acid to aqueous solutions of the sodium and potassium derivatives, (3) always when solutions of the ester are evaporated after being kept for some time, (4) by heating the β-modification above its m. p., and (5) by distillation of the ester under reduced pressure. It forms colourless leaflets or plates, m. p. 40—41°, develops in alcoholic solution with a small quantity of ferric chloride a deep bluish-violet coloration, gives a green, crystalline precipitate with a solution of copper acetate, slowly becomes blue after several minutes when shaken with decolorised magenta solution, and reacts with phenylcarbimide to form the expected *phenylcarbamate*, $NHPh·CO·O·CH:CPh·CO_2Me$, colourless needles, m. p. 133—134°. Mixed with an equal molecular quantity of aniline, it yields *methyl β-anilino-α-phenylacrylate*, $NHPh·CH:CPh·CO_2Me$, colourless needles, m. p. 113—114°, which is converted into 4-hydroxy-3-phenylquinoline at 265° with loss of

methyl alcohol. The ester reacts with *p*-xylidine to form a dark brown oil, which is converted by heating into *4-hydroxy-3-phenyl-5:8-dimethylquinoline*, yellowish-white needles, m. p. 254—256°. With an alcoholic solution of phenylhydrazine at 0°, the ester yields the *phenylhydrazone*, $NHPh\cdot N{:}CH\cdot CHPh\cdot CO_2Me$, stout prisms, m. p. 116—117°, together with formylphenylacetic acid hydrazide. In a similar manner, it reacts with diphenylhydrazine to form the *diphenylhydrazone*, $NPh_2\cdot N{:}CH\cdot CHPh\cdot CO_2Me$, colourless needles, m. p. 86—87°, whilst an aqueous solution of the sodium derivative of the ester reacts with semicarbazide hydrochloride to form the *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N{:}CH\cdot CHPh\cdot CO_2Me$, crystals, m. p. 159—160°.

In its general behaviour the α-modification behaves like a typical enol and is to be regarded as having the constitution

$$OH\cdot CH{:}CPh\cdot CO_2Me,$$

corresponding with the α-modification of the ethyl ester (*loc. cit.*).

The β-modification of the methyl ester can be prepared only in one way: by adding an aqueous solution of the sodium derivative as rapidly and as suddenly as possible to an excess of cold, not too dilute sulphuric acid. A spontaneous change of the α- into the β-modification has never been observed (unlike the ethyl ester, *loc. cit.*). The β-modification forms leaflets from warm benzene, m. p. 91—93°. It is much more soluble than the α-form in methyl alcohol and in water, but dissolves less readily than this in benzene and in light petroleum. A freshly prepared, cold alcoholic solution does not give a coloration with ferric chloride. The β-modification gives a precipitate with a solution of copper acetate only after long keeping (owing to change into the α-form), instantly recolours a decolorised solution of magenta, and reacts slowly and incompletely with phenylcarbimide to form the same phenylcarbamate as does the α-form.

The phenomena (decrease in the intensity of the coloration with ferric chloride; contraction in the volume of the solution) observed in an ethyl-alcoholic solution of the α-ethyl ester, which have been attributed to the change of the enol to an aldo-form, are repeated in the case of the methyl-alcoholic solution of the methyl ester. In this case, however, a definite *methyl alcoholate*, $C_{10}H_{10}O_3 + MeOH$, m. p. 89—92°, crystallises when the not too dilute solution is strongly cooled. The additive compound, which does not develop a coloration with ferric chloride, is formed from the β-modification after cooling the solution for one hour, but from the α-modification after twenty to twenty-four hours, and is therefore probably formed only from the β-modification. It can be recrystallised from warm benzene, but easily loses methyl alcohol by keeping in the air, by warming, and rapidly in a vacuum, the α-modification being obtained. The behaviour of an "old" methyl-alcoholic solution of the methyl ester with ferric chloride, copper acetate, and decolorised magenta solution is just what would be expected if the solution contained an alcoholate of the β-modification, which can be slowly decomposed by the reagent, yielding the α-modification. Michael and Fuller (A., 1912, i, 861) have directed attention to the

formation of additive compounds of the ethyl ester with methyl and with ethyl alcohol.

The constitutions of the two modifications of methyl formylphenylacetate are discussed at length. The α-form is undoubtedly an enol. The β-form presents difficulties. Some facts point to an aldo-form, others to a second, geometrically isomeric, enol form. Owing to the discovery of the alcoholates, all the evidence previously advanced in the case of the ethyl ester in favour of the aldo-form and based on the physico-chemical properties of alcoholic solutions loses in weight. On the other hand, since 1912 the properties of the true keto-forms of desmotropic substances have become better known, and in view of this knowledge the fact that the β-ester has about the same solubility in alkali hydroxide as the α-ester (A., 1912, i, 623) strengthens the view that the β-modification may be a second enol form. Moreover, Meyer has shown by his bromine method that the four modifications of the ethyl ester are unsaturated (A., 1912, i, 940), and the authors now show that both modifications of the methyl ester in freshly prepared methyl-alcoholic solution equally and almost quantitatively absorb bromine. These facts and the evidence of Scheiber and Herold's method of examination of the ethyl ester by means of ozone do not uphold the view that the β-modification is an aldo-form. Nevertheless, it must be acknowledged that the changes which characterise true aldehyde reactions, such as the restoration of the colour of decolorised magenta solution and the addition of methyl alcohol, occur more rapidly with the β- than with the α-modification. Weighing all the evidence, the authors incline at the present moment to the view that the two modifications of methyl formylphenylacetate (and also of the ethyl ester) are enols and examples of geometrical or *cis-trans*-isomerism, despite the facts that the β-form can under no conditions be made to develop a coloration with ferric chloride and that the two modifications behave so differently with copper acetate. C. S.

Mixed Anhydrides derived from Benzoylacrylic Acid. J. Bougault (*Compt. rend.*, 1917, **164**, 310—313).—A continuation of previous work (A., 1908, i, 791). The author has now condensed the two isomeric α-bromocinnamic acids with benzoylacrylic acid, by the addition of iodine in potassium iodide to a solution of their sodium salts with sodium phenyl*iso*crotonate in the presence of sodium carbonate. The stable form gives an *anhydride*, COPh·CH:CH·CO·O·CO·CBr:CHPh, m. p. 100°, and the labile form an isomeric *anhydride*, m. p. 125°. These anhydrides have properties similar to those of the four anhydrides previously described (*loc. cit.*). When heated at 100° with 50% acetic acid, they give benzoylacrylic acid and the respective α-bromocinnamic acids. Attempts to convert the anhydride, m. p. 125°, into the anhydride, m. p. 100°, were unsuccessful.

Further evidence is adduced in support of his theory as to the mode of formation of these anhydrides, in that γ-hydroxyphenylcrotonic acid, which is converted into benzoylacrylic acid by the

action of iodine in the presence of sodium carbonate, does not give a mixed anhydride with sodium benzoate under the above conditions, although benzoylacrylic acid is formed. W. G.

Preparation of Arylamides of 2-Hydroxynaphthalene-3-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294799; from *J. Soc. Chem. Ind.*, 1917, **36**, 286).—A mixture of 2-hydroxynaphthalene-3-carboxylic acid with a large excess of an aromatic amine is treated with phosphorus chloride, whereby the hydroxynaphthoyl chloride first formed reacts with the amine to form the arylamide. The yield is approximately quantitative. H. W.

Desmotropic Forms in the Series of Oxalacetic Ester Derivatives, especially of Ethyl Diphenylmethyloxalacetate [α-Oxalo-ββ-diphenylpropionate]. WILHELM WISLICENUS and KARL EBLE (*Ber.*, 1917, **50**, 250—262).—Although the enolic form of methyl oxalacetate is so much more favoured than the ketonic form that the isolation and preservation of the latter require special precautions (see Dieckmann, A., 1916, i, 820), it would appear from the usual chemical and physical measurements that the amount of the enol present in a methyl-alcoholic solution is unusually small. This is due to the fact that combination with the solvent takes place, and such an additive compound may be isolated.

It was anticipated that the ketonic form would be more stable in the case of solid esters having a heavy residue as a substituent of the methylene group, and two examples are described in which the ketonic structure is actually preferred, namely, diethyl α-oxalo-ββ-diphenylpropionate and diethyl α-oxalo-β-diphenylenepropionate.

Ethyl ββ-diphenylpropionate (the acid is made by condensing cinnamic acid with benzene in the presence of aluminium chloride) condenses with ethyl oxalate in the presence of potassium ethoxide to form the *potassium* compound of *diethyl α-oxalo-ββ-diphenylpropionate*, which crystallises in small rods. The unstable *enol* is precipitated if the solution of this salt is stirred into cold sulphuric acid; it crystallises from a benzene–light petroleum mixture in colourless, rhombic tablets, m. p. 99—101°. The *ketone* modification, $CO_2Et\cdot CO\cdot CH(CHPh_2)\cdot CO_2Et$, is obtained by crystallising the enol from alcohol, or by the action of carbon dioxide on a solution of the potassium salt; it crystallises in bundles of long rods, m. p. 60—61°. The ester is readily hydrolysed by 20% potassium hydroxide to oxalic and diphenylpropionic acids, but is indifferent to the action of 20% sulphuric acid at 150°. It loses carbon monoxide at 200°, forming ethyl diphenyl*iso*succinate, m. p. 57—60° (Henderson, T., 1891, **59**, 731). The ester also forms an additive compound with phenylhydrazine (rhombic leaflets, m. p. 112°), which changes on heating into the *phenylhydrazone*, silky, yellow needles, m. p. 90—91°, and this is

further transformed by heating at 195—200° into *ethyl 1-phenyl-4-diphenylmethylpyrazol-5-one-3-carboxylate*,

$$NPh<\begin{matrix}N{=}C\cdot CO_2Et \\ CO\cdot CH\cdot CHPh_2\end{matrix},$$

which crystallises in almost colourless, rhombic leaflets, m. p. 148—149°.

The above potassium salt is very sensitive to the action of moisture, changing readily into the *potassium* salt of *ethyl α-oxalo-ββ-diphenylpropionate*, $CO_2K\cdot CO\cdot CH(CHPh_2)\cdot CO_2Et,H_2O$, which crystallises in bundles of filaments, m. p. 200° (decomp.). The free *ester acid* may be obtained from this salt or by shaking the above enolic or ketonic ester with 10% sodium carbonate until dissolution takes place, and then acidifying. It has m. p. 96—97° and crystallises from benzene with $\frac{1}{3}C_6H_6$, m. p. 90—92°. It also forms a *phenylhydrazone*, greenish-yellow needles, m. p. 190—192°, which changes on heating at 190—200° into *1-phenyl-4-diphenylmethylpyrazol-5-one*, prisms or leaflets, m. p. 220—221° (compare the above pyrazolone).

Fluorene-9-acetic acid may be prepared in one operation, starting with fluorene, ethyl oxalate, and ethyl bromoacetate (compare Mayer, A., 1913, i, 1171). It crystallises in flat, silky needles, m. p. 138—139°. The *ethyl* ester, b. p. 214°/12 mm., condenses with ethyl oxalate in the presence of potassium ethoxide to form the *potassium* compound of *diethyl α-oxalo-β-diphenylenepropionate*, which crystallises in colourless needles. The free *ester*, $\begin{matrix}C_6H_4 \\ | \\ C_6H_4\end{matrix}>CH\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et$, can be obtained as an enol, but it changes even by crystallisation from cold benzene into the ketonic form, which separates in bundles of needles, m. p. 86—88°.

J. C. W.

Occurrence of Mellitic Acid. EDMUND O. VON LIPPMANN (*Ber.*, 1917, **50**, 236—238).—Some years ago (A., 1895, i, 164) the author reported the occurrence of mellitic acid in a black, humus-like deposit found in a disused conduit in a sugar refinery. When an old copper conduit was dismantled recently, a similar deposit was found.

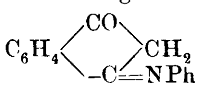
In connexion with the author's view that the formation of mellitic acid represents a gradual, but thorough, process of oxidation, another accidental production of large crystals of aluminium mellitate, $C_{12}H_{12}Al_2,18H_2O$, "honey stone," is reported. A load of aluminous sludge from a plant for sewage treatment was deposited on a heap of brown coal rubbish, on the top of which a small plank was lying. After two years, when the refuse was being removed, the crystals of "honey stone" were found in a hollow under the wood. J. C. W.

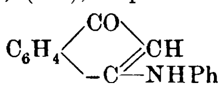
Preparation of Protocatechualdehyde. L. SCHMIDT (D.R.-P., 295337, addition to D.R.-P., 278778; from *J. Soc. Chem. Ind.*, 1917, **36**, 306).—The piperonal diacetate, obtained from piperonal

as described in the original patent (A., 1915, i, 682), is treated with chlorine, and the resulting dichloropiperonal diacetate is decomposed with water. Derivatives of chloroacetic acid are not formed during the chlorination. H. W.

Indandione and Bindone. I. Aniline Derivatives of Indandione. WILHELM WISLICENUS and HUGO PFANNENSTIEL (*Ber.*, 1917, **50**, 183—189).—The condensation products of indandione (diketohydrindene) and bindone (anhydrobisdiketohydrindene) can be resolved by treatment with aniline into simple derivatives of indandione. As a preliminary to a series of communications on this reaction, the anils of indandione are now described.

If indandione is dissolved in warm aniline and dilute acetic acid is added to the cold solution, *indandione monoanil* (I) soon separates, in yellowish-green, rectangular leaflets, m. p. 208° (decomp.). This forms unstable salts with mineral acids, in which it conforms to type (II), and also with alkali hydroxides, in which the remaining structure, (III), is probable.


(I.)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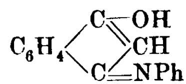

(III.)

Schlossberg (A., 1900, i, 665) ascribed to the free substance formula (II).

A deep red solution containing the acetate of a dianil is obtained if indandione is heated with aniline (20 parts) and glacial acetic acid (5 parts). When this is mixed with dilute acetic acid and poured into brine, the hydrochloride is precipitated, and from this the free base is obtained by treatment with dilute sodium hydroxide. *Indandione dianil*, $C_6H_4<\genfrac{}{}{0pt}{}{C(:NPh)}{C(:NPh)}>CH_2,H_2O$, crystallises in brownish-red, stout prisms, m. p. 180—181°, loses water at 100°, and then has m. p. 176—177°. The *hydrochloride*, B,HCl,H_2O, forms dark red, glistening prisms, which sinter at 253—260°; the anhydrous salt is somewhat paler in colour. Two *sulphates* are described: $B_2,H_2SO_4,2H_2O$, dark red, rhombic crystals, and B,H_2SO_4, microscopic, red needles. The *diacetate* is also dark red, and is quickly hydrolysed by water.

These anils are completely hydrolysed to indandione and aniline by warming with excess of dilute hydrochloric acid. With certain quantities of acid, however (1HCl to 2 mols. of the monoanil or 3HCl to 2 mols. of the dianil), the blue anil of bindone is formed (Liebermann, A., 1898, i, 200, and following abstract). The diacetate of the above dianil is produced, on the other hand, when bindone is warmed with aniline (6 parts) and glacial acetic acid (1 part) for some time, thus:

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C:C<\genfrac{}{}{0pt}{}{C_6H_4}{CH_2}>CO + 4C_6H_5\cdot NH_2 + 4MeCO_2H =$$
$$2C_{21}H_{16}N_2,2MeCO_2H + 3H_2O.$$

J. C. W.

Indandione and Bindone. II. Action of Aromatic Amines on Bindone. WILHELM WISLICENUS and HERMANN SCHNECK (*Ber.*, 1917, **50**, 189—198).—The production of blue colouring matters from bindone by the action of amines was briefly described by Liebermann (A., 1898, i, 200). Contrary to the original statement, it is found that methyl- and ethyl-anilines behave like primary bases. No amines react, however, which are too feebly basic to bring about the enolisation of bindone, and it is usually noticed that before the blue colour appears there is a stage which represents the violet-red salts of the enol. The blue compounds are consequently designated anilides of *bindenol*,

$$C_6H_4<{CO \atop CO}>C:C<{C_6H_4 \atop -CH}>C\cdot OH.$$

Bindenylaniline, $C_{24}H_{15}O_2N,H_2O$, crystallises in bundles of dark blue, filamentous needles, m. p. 224—225°, and forms a *dihydrochloride*, B,2HCl, in olive-green, elongated leaflets. Bindone does not react with sulphanilic acid in glacial acetic acid unless sodium acetate is added, and then it forms *sodium* p-*bindenylaminobenzenesulphonate*,

$$C_6H_4<{CO \atop CO}>C:C<{C_6H_4 \atop -CH}>C\cdot NH\cdot C_6H_4\cdot SO_3Na,$$

in tufts of deep blue filaments, decomp. above 230°.

Bindenylethylaniline, $C_6H_4<{CO \atop CO}>C:C<{C_6H_4 \atop -CH}>C\cdot NEtPh$, crystallises in blackish-blue prisms, m. p. 181—182°, and forms a *monohydrochloride*, matted needles, and a *dihydrochloride*, greenish-yellow, elongated, six-sided tablets.

Dimethyl- and diethyl-aniline merely enolise bindone under the above conditions, but condensation of another kind takes place under the influence of zinc chloride. p-*Bindenylphenyldimethylamine*, $C_6H_4<{CO \atop CO}>C:C<{C_6H_4 \atop -CH}>C\cdot C_6H_4\cdot NMe_2$, may be isolated from the dark green fusion obtained in this way in the form of irregular, green leaflets, m. p. 234—235°. Diphenylamine also gives a green fusion, and does not behave like the above secondary anilines. J. C. W.

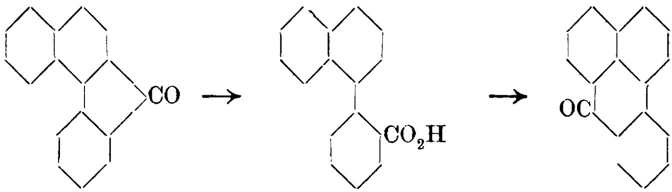
3 : 4-Benzofluorenone. ALFRED SCHAARSCHMIDT (*Ber.*, 1917, **50**, 293—294. Compare Pfeiffer, this vol., i, 145).—The ketone which Pfeiffer described in 1907 must have been the metastable form of 3 : 4-benzofluorenone, or a different compound altogether. J. C. W.

A New Benzanthrone Synthesis. ALFRED SCHAARSCHMIDT [with EUGEN GEORGEACOPOL] (*Ber.*, 1917, **50**, 294—303).—When 3 : 4-benzofluorenone is fused with potassium hydroxide, the ring bearing the ketone group can be ruptured in two ways, giving different carboxylic acids, thus:

$$CO<{C_{10}H_6 \atop |\atop C_6H_4} \longrightarrow CO_2H\cdot C_{10}H_6\cdot C_6H_5 \quad \text{or} \quad C_{10}H_7\cdot C_6H_4\cdot CO_2H.$$

If these acids were dissolved in concentrated sulphuric acid, the phenylnaphthoic acid could only give the original ketone again,

whereas the naphthyl residue in the naphthylbenzoic acid might perhaps rotate, and so give rise to benzanthrone, thus:

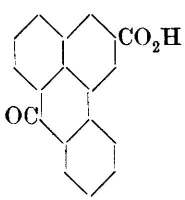


The fact that the sulphuric acid solution is fluorescent shows that benzanthrone is indeed formed. The reaction represents a new synthesis of benzanthrone, and has therefore been extended to derivatives of 3:4-benzofluorenone. In the case of the 1-carboxy- and 1-benzoyl-derivatives, it is found that the rupture of the link between the carbonyl group and the naphthalene ring and the subsequent condensation to benzanthrones are operations which proceed almost quantitatively.

3:4-Benzofluorenone-1-carboxylic acid (A., 1916, i, 47) is heated with potassium hydroxide at 230—235°, and so converted into 1-*phenylnaphthalene*-o-3-*dicarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot C_{10}H_6\cdot CO_2H,$$

which forms glistening crystals, m. p. 288°. This is transformed into *benzanthronecarboxylic acid* (annexed formula), bright yellow needles, m. p. 347°, by dissolving it in concentrated sulphuric acid or by converting it into the chloride by means of phosphorus pentachloride, warming this with aluminium chloride in carbon disulphide, and boiling the acid chloride so formed with dilute potassium hydroxide. *Benzoylbenzanthrone*, slender, pale yellowish-green needles, m. p. 206°, is obtained by condensing the chloride of either the above mono- or di-carboxylic acid with benzene by the agency of aluminium chloride.



1-Benzoyl-3:4-benzofluorenone may also be converted by alkaline fusion into 3-*benzoyl*-1-*phenylnaphthalene*-o-*carboxylic acid* (o-3-*benzoyl*-α-*naphthylbenzoic acid*),

$$COPh\cdot C_{10}H_6\cdot C_6H_4\cdot CO_2H,$$

m. p. 280—282°.

1-Phenylnaphthalene-*o*-3-dicarboxylic acid forms a *bromo*-compound, slender, yellowish-grey crystals, m. p. 282°, which may be condensed to *bromobenzoylbenzanthrone*, yellowish-green crystals, m. p. 242°.

With the formation of benzanthronecarboxylic acid, there is no possibility of further intramolecular condensations, but two molecules of this acid may unite through the naphthalene residues. A small quantity of a very powerful violet dye, which is most probably a compound of such a type, is formed during the alkaline fusion. The production of this dye in quantity and its characteristics will be described later. J. C. W.

Chrysarobin. III. O. Hesse (*Annalen*, 1917, **413**, 350—378. Compare A., 1912, i, 277).—The first part of the paper deals with a re-examination of the constituents of commercial chrysarobin and with the behaviour towards hydriodic acid of its mixtures with chrysophanic acid and emodin methyl ether. The work was undertaken in consequence of Tutin and Clewer's description of the constituents of commercial chrysarobin (P., 1913, **20**, 285), in particular, of dehydroemodinanthranol monomethyl ether. Tutin and Clewer assert that the author overlooked this, because by his method of separation by demethylation by hydrochloric or hydriodic acid it would be converted into emodinol. The author retaliates by asking how hydrochloric acid could effect such a conversion, and by stating that if hydriodic acid effected such a reduction iodine must be liberated, a phenomenon which he and Tutin and Clewer have not observed.

Directions are given for the preparation of pure chrysarobin or chrysarobinum purum, by which the author means officinal chrysarobin or chrysarobinum venale freed from anthraquinones and from the constituents insoluble in light petroleum. It consists of chrysophanol and emodinol and their méthyl ethers. Chrysarobol is the only crystalline substance which has been isolated from the constituents of commercial chrysarobin insoluble in light petroleum.

The investigation shows that, although commercial chrysarobins from different sources vary, occasionally considerably, in their composition, chrysophanol, emodinol, and its methyl ether together constitute usually more than 80% of the substance, substances insoluble in light petroleum, chrysophanic acid, emodin and its methyl ether together constitute usually 10% or less, whilst loss and substances not definitely characterised represent about 10%. The presence of ararobinol and dehydroemodinanthranol monomethyl ether has not been detected. C. S.

The Aloins. E. Léger (*Ann. Chim.*, 1916, [ix], **6**, 318—381).—A résumé of work already published (compare A., 1900, i, 512; 1902, i, 549, 685; ii, 484; 1903, i, 356; 1904, i, 907; 1905, i, 532; 1907, i, 545, 631; 1908, i, 40, 980; 1910, i, 463, 543; 1911, i, 140, 734). W. G.

New Active Principles in the Genus Xanthoxyllum. H. Bocquillon (*Rép. Pharm.*, 1917, **28**, 66; from *Pharm. J.*, 1917, **98**, 275).—In continuation of previous work, the occurrence of crystalline neutral principles in different members of the genus *Xanthoxyllum* has been established, and these substances have been shown to be lactones. From *X. caribœum*, light petroleum extracts the lactone, *carixanthide*, $C_{12}H_{24}O$, colourless needles, m. p. 285°. Similarly, *X. carolianum* yields *carolixanthide*, needles, m. p. 119°. The occurrence in the seeds of *X. piperitum* of the crystalline substance, m. p. 80°, isolated many years ago by Stenhouse (*Annalen*, 1854, **89**, 251; 1857, **104**, 236), is confirmed, as well as the presence of α-xanthoxylin, colourless plates, m. p. 162°, and β-xanthoxylin, m. p. 187°, in the seeds of *X. octroxylum*, as

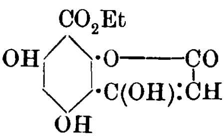
recorded by Leprince (A., 1912, ii, 479). All these substances are accompanied by fixed or volatile oils. H. W.

1 : 1 : 4-Trimethylcoumaranone and 3 : 6-Dimethylchromanone (3 : 6-Dimethyl-1 : 4-benzopyrone). K. VON AUWERS (*Ber.*, 1917, **50**, 221—224. Compare A., 1914, i, 1136).—Genuine 1 : 1 : 4-*trimethylcoumaranone*, b. p. 120°/15 mm., D_4^{20} 1·071, n_D^{20} 1·540, *semicarbazone*, m. p. 202—203°, has now been obtained by methylating 1 : 4-dimethylcoumaranone by means of methyl iodide and sodamide. The compound, which was obtained by the action of diethylaniline on *m*-α-bromo*iso*butyryl-*p*-cresol, can also be prepared by warming an aqueous-alcoholic solution of *m*-β-chloro*iso*butyryl-*p*-cresol with sodium carbonate. It therefore has the alternative structure of 3 : 6-*dimethyl*-1 : 4-*benzopyrone*, and its formation by the older method involves the production of an unsaturated ketone, thus:

$$OH\cdot C_6H_3Me\cdot CO\cdot CMe_2Br \longrightarrow OH\cdot C_6H_3Me\cdot CO\cdot CMe{:}CH_2 \longrightarrow C_6H_3Me\begin{cases}CO\cdot CHMe \\ O\text{—}CH_2\end{cases}$$

J. C. W.

Preparation of Benzylidene Compounds of Ethyl 4 : 5 : 7-Trihydroxycoumarin-8-(or 6)-carboxylate. ADOLF SONN (*Ber.*, 1917, **50**, 138—144).—Leuchs and Sperling have shown (A., 1915, i, 141) that the "lactone" which Jerdan obtained from ethyl acetonedicarboxylate (T., 1897, **71**, 1111) is in all probability a hydroxycoumarin derivative of the annexed formula. As a "benzotetronic acid" it should therefore condense very readily with aldehydes (compare Anschütz, A., 1909, i, 660), and this is found to be the case. The following 3-benzylidene derivatives were obtained by merely mixing hot alcoholic solutions of the ester and aldehyde and cooling the liquid; *anisylidene*-, a mass of fibrous, orange-yellow needles, m. p. 208°; p-*hydroxybenzylidene*-, m. p. 194—195°; *salicylidene*-, almost colourless tufts, m. p. 180°; *vanillylidene*-, orange-red sheaves, m. p. 247°; *piperonylidene*-, orange-yellow tufts, m. p. 200°; o-p-*dihydroxybenzylidene*-, brownish-yellow, granular aggregates of prisms, decomp. above 200°. The first two were reduced by means of zinc dust and glacial acetic acid to the 3-β-p-*methoxyphenylethyl*- (elongated, colourless tablets, m. p. 235°) and 3-β-p-*hydroxyphenylethyl*-derivatives (colourless plates, m. p. 215°) respectively. J. C. W.



Thiophen Series. VIII. Some Derivatives of 2-Acetothienone. WILHELM STEINKOPF and DORA JAFFÉ (*Annalen*, 1917, **413**, 333—342).—Contrary to experience in the benzene series the simultaneous production of two isomerides in the thiophen series has been very seldom observed.

The nitration of 2-acetothienone, first done by Meyer and Peter in 1884–1885, is effected with much better results by adding slowly

a solution of nitric acid, D 1·52, in acetic anhydride to a solution of 2-acetothienone in the same solvent cooled in a freezing mixture, the temperature being kept below $-6°$ during the addition. The two nitro-2-acetothienones produced have m. p. 88—89° and 127° respectively (not 86° and 122·5°, as recorded in the literature). Attempts to discover a more convenient method of separating the two isomerides have been unsuccessful, and the orientation of the nitro-groups has not yet been settled owing to experimental difficulties.

The nitro-2-acetothienone, m. p. 88°, is reduced by tin and warm concentrated hydrochloric acid to the *stannichloride* of *amino-2-acetothienone*, $2COMe·C_4H_2S·NH_2,H_2SnCl_6$, brownish-orange crystals, m. p. 202—203° (decomp.), from which the *acetylamino-2-acetothienone*, $NHAc·C_4H_2S·COMe$, brown crystals, m. p. 270—271°, can be obtained.

The nitro-2-acetothienone, m. p. 127°, forms an *oxime*,

$$NO_2·C_4H_2S·CMe:NOH,$$

crystals, m. p. 127°, but the isomeride of lower m. p. yields a mixture of several substances under the same conditions. Attempts to apply the Beckmann transformation have been unsuccessful.

2-Acetothienone forms a *semicarbazone*, leaflets, m. p. 190—191°, *benzoylhydrazone*, colourless crystals, m. p. 187—188°, p-*nitrophenylhydrazone*, stout, dark red crystals, m. p. 181—182°, *aminoguanidino*-derivative, $C_4H_3S·CMe:N·NH·C(NH_2):NH$, small needles, m. p. 83—83·5° (*picrate*, $C_7H_{10}N_4S,C_6H_3O_7N_3$, yellow crystals, decomp. 247—248°, with previous sintering and darkening), and the condensation *derivative* with *p*-phenetidine, $C_4H_3S·CMe:N·C_6H_4·OEt$, brownish-golden-yellow needles, m. p. 90·5—91°.

2-Acetothienoneoxime reacts with chloral in the smallest possible quantity of cold benzene to form *chloral-2-acetothienoneoxime*, $C_4H_3S·CMe:N·O·CH(OH)·CCl_3$, colourless crystals, m. p. 87°.

C. S.

Thiophen Series. IX. New Method of Preparation of Thienyl Ketones. WILHELM STEINKOPF (*Annalen*, 1917, **413**, 343—349).—Lecher's method (A., 1913, i, 1166) of preparing ketones of the benzene series is found to be even more effective in the thiophen series; acid chlorides of the aliphatic or of the aromatic series may be employed, and hydrogen chloride is evolved at a lower temperature, so that the reaction can be effected in open vessels.

Some light is thrown on the catalytic activity of the phosphoric oxide by the discovery that acid anhydrides can replace acid chlorides. Hydrogen chloride, therefore, is not essential to the catalysis. When an acid anhydride is used, the reaction proceeds, in the author's opinion, with the intermediate formation of an acylmetaphosphoric acid (compare acetylsulphuric acid): (1) $P_2O_5 + 2Ac_2O = 2PO_2·OAc$, (2) $PO_2·OAc + C_4H_4S = C_4H_3S·COMe + PO_2·OH$, and (3) $PO_2·OH + PO_2·OAc = P_2O_5 + CH_3·CO_2H$. When an acid chloride is used, equation (1) becomes $P_2O_5 + CH_3·COCl = PO_2·OAc + PO_2Cl$, and (3) becomes $PO_2·OH + PO_2Cl = P_2O_5 + HCl$.

The acetylmetaphosphoric acid seems not to be formed from metaphosphoric acid itself, as the latter cannot be used in place of phosphoric oxide.

By this method thiophen and about 2% of its weight of phosphoric oxide react with acetyl chloride at 98—130° to give 52% of the theoretical yield of 2-acetothienone (the same yield is obtained with acetic anhydride at 140°), with chloroacetyl chloride at 130—140° to give ω-chloro-2-acetothienone in poor yield, with benzoyl chloride at 120—125° to give phenyl 2-thienyl ketone, and with *o*-toluoyl chloride at 130—140° to give *o*-tolyl 2-thienyl ketone.

Benzene, acetic anhydride, and phosphoric oxide at 100—140° do not yield acetophenone. C. S.

Stereochemistry of Rhodanines. I. STEN KALLENBERG (*Ber.*, 1917, **50**, 90—100).—The general characteristics of the group of substances now known as rhodanines have been established chiefly by Andreasch and his co-workers. Among other reactions, it has been shown that condensations with aldehydes at the carbon atom numbered 5 can be readily induced (compare Andreasch, and also Stieger, this vol., i, 171). This fact suggests that rhodanines can behave as thiazolines (II) as well as thiazolidines (I), which, of course, would be expected from analogies. Since carbon atom 5 is

$$NR<\begin{matrix}CO\cdot CHR'\\ CS-S\end{matrix} \qquad\qquad NR<\begin{matrix}C(OH)\colon CR\\ CS—S\end{matrix}$$

(I.) (II.)

asymmetric in formula (I), but not in (II), it should therefore be possible to decide whether one structure is favoured before the other. To this end the author has applied Holmberg's methods for preparing rhodanines (A., 1910, i, 361) to optically active materials, but he finds that, although the solutions remain active up to the last stage, the isolated rhodanines are always inactive. It appears, therefore, that structure (I) is only transient.

d-Trithiocarbodipropionic acid, $CS(S\cdot CHMe\cdot CO_2H)_2$, prepared by the resolution of the inactive acid (A., 1905, i, 325), was warmed with aniline and water, but the 3-phenyl-5-methylrhodanine so formed was inactive. It was considered that heating was detrimental, so this method was abandoned.

The alternative method required optically active halogeno-acids. *l*-β-Bromosuccinamic acid, $[\alpha]_D^{18}$ $-70\cdot03°$, was prepared for this purpose by the interaction of potassium bromide, sodium nitrite, 3*N*-sulphuric acid, and asparagine. Incidentally, i-β-*iodosuccinamic acid*, long prisms, m. p. 118—120°, was prepared from this by the action of an acetone solution of sodium iodide, the racemisation being in accordance with Westerlund's experience (A., 1915, i, 771).

When a solution of potassium ethyldithiocarbamate, prepared by mixing potassium hydroxide, ethylamine, and carbon disulphide, is mixed with *l*-β-bromosuccinamic acid, neutralised with sodium carbonate, and then acidified after some hours, d-β-*ethyldithiocarbamylsuccinamic acid* (III) separates in small leaflets, m. p. 112—113°, $[\alpha]_D$ $+55\cdot6°$. This readily undergoes dehydration to the rhodanine, for example, when an alkaline solution is left for some

time. 3-*Ethylrhodanine*-5-*acetamide* (IV) is a pale yellow, granular mass, m. p. 107—108°, and is optically inactive.

$$NHEt\cdot CS\cdot S\cdot CH<\begin{matrix}CO_2H\\CH_2\cdot CO\cdot NH_2\end{matrix} \qquad NEt<\begin{matrix}C(OH):C\cdot CH_2\cdot CO\cdot NH_2\\CS\text{----}S\end{matrix}$$

(III.) (IV.)

The rhodanine dissolves in dilute sodium hydroxide to give a deep red solution, from which sulphuric acid precipitates inactive *β-ethyldithiocarbamylsuccinamic acid* in colourless leaflets, m. p. 108—109°, which can also be obtained from *i*-β-iodosuccinamic acid as above.

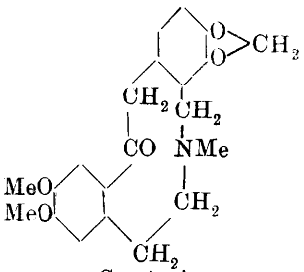
3-*Phenylrhodanine*-5-*acetamide*, thin, greenish-yellow tablets, m. p. 171—173°, is formed from either halogenosuccinamic acid, the intermediate hydrate being stable only in the form of its salts.

1-β-*Diethyldithiocarbamylsuccinamic acid*,

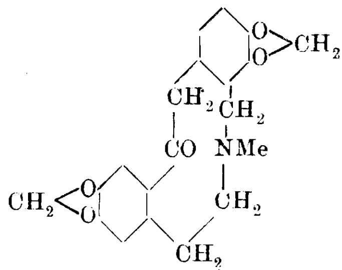
$$NEt_2\cdot CS\cdot S\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2,$$

is made in the same way, starting from diethylamine. It forms small prisms, m. p. 126—128°, $[\alpha]_D$ −18·8°, and yields an *ethyl ester*, m. p. 85—86°, which is inactive. When the aqueous solution is boiled, with or without acids, it suffers hydrolysis, *i-β-diethyldithiocarbamylsuccinic acid*, m. p. 109—111°, being formed, whilst hydrolysis with alkalis leads to the production of fumaramic acid, m. p. 216—218°. On treatment with alkaline permanganate in the cold, one sulphur atom is exchanged for oxygen, d-*β-diethylthiocarbamylsuccinamic acid*, $NEt_2\cdot CO\cdot S\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$, being formed, in colourless needles, m. p. 144—145° (decomp.), $[\alpha]_D$ +74·3°. Inactive *β-diethyldithiocarbamylsuccinamic acid*, m. p. 131—132° (decomp.), is obtained from β-iodosuccinamic acid, it yields inactive *β-diethylthiocarbamylsuccinamic acid*, nodules of prisms, m. p. 139—140°. J. C. W.

Cryptopine and Protopine. WILLIAM HENRY PERKIN, jun. (T., 1916, **109**, 815—1028).—The paper is mainly occupied with the results of an exhaustive and laborious investigation of the degradation and other products of cryptopine with a view to establishing its constitution. The only degradation product obtained previously was *m*-hemipinic acid, showing the presence of a dimethoxybenzene nucleus, but there was strong reason to believe that there was also present a second benzene nucleus to which a methylenedioxy-group was attached. In the present investigation the alkaloid was subjected to the action of a long series of oxidising and hydrolytic agents under a great variety of conditions, but in every case the piperonyl ring was completely destroyed, and the only substances that could be isolated were derived from the dimethoxybenzene nucleus. This difficulty was at length overcome by reducing *cryptopine methosulphate* with sodium amalgam, when *methyltetrahydrocryptopine* was formed, and by dehydration with acetyl chloride was converted into *anhydromethyltetrahydrocryptopine*, from the oxidation products of which piperonyl derivatives could be isolated. Working on this and other lines, many series of derivatives of cryptopine and of the closely related protopine were prepared, and from the results the annexed formulæ were deduced for the two alkaloids:



Cryptopine.

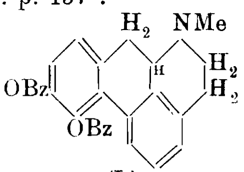


Protopine.

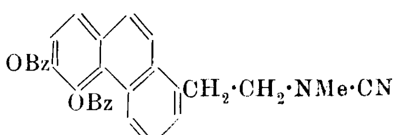
The evidence brought forward to prove the nature and relative positions of the various groups and rings cannot be recapitulated here; it is summarised by the author in the introduction to the paper (pp. 819–877), to which reference must be made. In the course of the investigation a very large number of new substances were prepared, and detailed descriptions of these and of their relationships will be found in the experimental section of the paper.

T. H. P.

The Morphine Alkaloids. V. J. VON BRAUN and E. AUST (*Ber.*, 1917, **50**, 43—44).—The constitution of *apo*morphine being known, it might be expected to behave differently from morphine towards cyanogen bromide. Instead of losing the *N*-methyl group, it should, in the light of the experience recently gained with hydrogenated *iso*quinolines (this vol., i, 162), suffer rupture of the ring. Dibenzoyl*apo*morphine (I) does behave in this way, yielding the *compound* II as an optically inactive, crystalline powder, m. p. 157°.



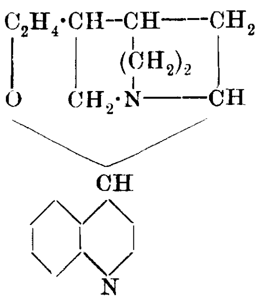
(I.)



(II).

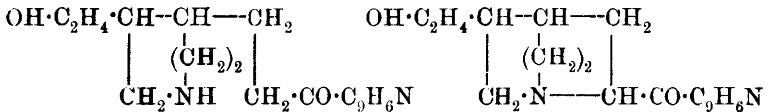
J. C. W.

Cinchona Alkaloids. XVIII. α-*iso*Cinchonine. PAUL RABE and BRUNO BÖTTCHER (*Ber.*, 1917, **50**, 127—133).—In his comprehensive survey of the chemistry of the cinchona alkaloids (A., 1906, i, 762) Koenigs suggested that α-*iso*cinchonine is an oxide of the annexed formula. This is now confirmed, but the question whether the C_2H_4 residue is $-CH_2{\cdot}CH_2-$ or $:CHMe$ is left open. α-*iso*Cinchonine is therefore to be regarded as the internal oxide of a hydroxydihydrocinchonine.



α-*iso*Cinchonine is recovered unchanged after boiling with dilute hydrochloric acid for several hours, but with dilute acetic or phosphoric acid, in the dark and in the

absence of air, it is converted into a toxine, *hydroxydihydrocinchonicine* (I), which crystallises in rectangular plates, m. p. 125°, $[\alpha]_D^{17}$ $-24 \cdot 9°$, and forms an amorphous phenylhydrazone and a *picrate*, red prisms, m. p. 220—221° (decomp.). The toxine reacts with sodium hypobromite to form a bromo-imine, which condenses in the presence of sodium ethoxide to *hydroxydihydrocinchoninone* (II). This crystallises in pale yellow needles, m. p. 170°,



(I.) (II.)

$[\alpha]_D^{15}$ $+36°$, after one hour, $+69 \cdot 2°$ (constant) after twenty-two hours, and forms a *picrate*, in many-sided, yellow platelets, m. p. 222—224°. J. C. W.

Preparation of 2 : 6-Dimethylpiperidines Substituted in the 2-Position, including their 1-Methyl Derivatives. H. M. JUDD and G. A. R. KON (Brit. Pat., 1916, 103541; from *J. Soc. Chem. Ind.*, 1917, **36**, 353).—By using sodium in amyl alcohol instead of sodium or aluminium amalgam for reducing the corresponding 4-piperidones, the resulting piperidine derivative is almost entirely the physiologically active isomeride instead of a mixture of two isomerides. A better yield is obtained and the trouble of isomerising the mixture is avoided. Details are given of the reduction of vinyldiacetoneamine (2 : 2 : 6-trimethylpiperidone). H. W.

Rupture of the Hydrogenated Indole and Quinoline Rings by Reduction. IV. 2-Methyltetrahydroquinoline. J. VON BRAUN and L. NEUMANN (*Ber.*, 1917, **50**, 50—55. Compare this vol., i, 167).—It has already been shown that when the quaternary methochloride of dihydroindole is treated with sodium amalgam, rupture of the pyrrole ring between the nitrogen atom and the chain of methylene groups takes place to a certain extent, and that this type of reduction is particularly favoured if there is a methyl group attached to the carbon atom adjacent to the nitrogen atom. In the case of tetrahydroquinoline, however, such a reaction has not yet been observed. Either the ring is ruptured between the nitrogen atom and the benzene nucleus or else one of the *N*-methyl groups is eliminated. It was considered to be worth while, however, to test whether a methyl group in position 2 would be favourable, as in the case of the indole derivatives, but it is found that 2-methyltetrahydroquinoline behaves exactly like tetrahydroquinoline. There appears, therefore, to be a fundamental difference between the indole and quinoline rings in this respect.

2-Methylquinoline is readily converted by successive stages into trimethyltetrahydroquinolinium chloride, and this yields a greater amount of the reduction products than is obtained in the case of tetrahydroquinoline. The mixture consists of 1 : 2-dimethyltetrahydroquinoline (40%), which is removed as the non-volatile compound with formaldehyde, and *γ-dimethylaminobutylbenzene*,

$$CH_2Ph \cdot CH_2 \cdot CHMe \cdot NMe_2$$

(60%), which is volatile in steam. This base is a limpid liquid, b. p. 124—125°/20 mm., which forms a *hydrochloride*, m. p. 127—129°, a flesh-red *platinichloride*, m. p. 173°, a *picrate*, m. p. 113—114°, and a *methiodide*, m. p. 128°.

γ-*Cyanomethylaminobutylbenzene*,

$$CH_2Ph\cdot CH_2\cdot CHMe\cdot NMe\cdot CN,$$

b. p. 188—189°/24 mm., is formed when the dimethyl base is treated with cyanogen bromide, together with a small amount of the hygroscopic *methobromide* of the dimethyl base, m. p. 142°. When the cyano-compound is heated with hydrochloric acid at 170°, it is hydrolysed to γ-*methylaminobutylbenzene*, which has b. p. 112—114°/14 mm., and yields a *hydrochloride*, m. p. 94—96°, an orange-red *platinichloride*, m. p. 169°, and a *phenylthiocarbamide*, m. p. 103—104°.

When the oily benzoyl derivative of this base is melted with phosphorus pentachloride and then distilled, up to 115° under ordinary pressure, then to 185° under 20 mm., the primary chloride, $CH_2Ph\cdot CH_2\cdot CHMe\cdot NMe\cdot CPhCl_2$, decomposes to a slight extent into methyl chloride and the imino-compound,

$$CH_2Ph\cdot CH_2\cdot CHMe\cdot N{:}CPhCl,$$

but mainly into benzonitrile, methyl chloride, and γ-chlorobutylbenzene. When treated with water, the imino-chloride changes into γ-benzoylaminobutylbenzene (Harries, A., 1903, i, 815), and the benzonitrile and γ-chlorobutylbenzene can then be removed by a current of steam. The nitrile is then separated by hydrolysis with alcoholic hydrochloric acid in the cold, leaving γ-*chlorobutylbenzene*, $CH_2Ph\cdot CH_2\cdot CHMeCl$, as a pleasant-smelling oil, b. p. 113—116°/16 mm. This readily yields α-methylhydrindene, b. p. 183—185° (not quite pure), when warmed with aluminium chloride and light petroleum, which is an interesting reaction, in view of the fact that the closely related γ-chloropropylbenzene does not yield hydrindene (A., 1912, i, 435). J. C. W.

4-Quinolyl Ketones. III. Synthesis of Substances Related to Quinine. Paul Rabe, Richard Pasternack, and Karl Kindler (*Ber.*, 1917, **50**, 144—156. Compare A., 1913, i, 513, 514).—The synthesis of some simple 4-quinolyl ketones has already been described. Of the three methods which were tested, the best is the condensation of 4-quinolylcarboxylates with esters, by Claisen's method, followed by ketone hydrolysis. If the 4-quinoloylacetic esters or the ketones are treated with bromine, the aliphatic chains are attacked, and the derivatives so formed can then be condensed with amines. The αβ-amino-ketones may then be reduced to amino-alcohols, which are more or less related to the cinchona alkaloids, according to the nature of the original quinoline derivative and the amine employed, thus: $Q\cdot CO\cdot CH_2R \longrightarrow Q\cdot CO\cdot CHRBr \longrightarrow Q\cdot CO\cdot CHR\cdot N< \longrightarrow Q\cdot CH(OH)\cdot CHR\cdot N<$.

The synthesis of such amino-alcohols is being rapidly developed, in order, if possible, to decide on what groupings or structure the physiological properties of quinine depend. The closing of the quinuclidine ring is not yet described, but the necessary conditions

will not be difficult to find, a good deal of encouragement having been received already.

Ethyl quinate is condensed with ethyl acetate to form *ethyl 6-methoxy-4-quinoloylacetate*, $OMe\cdot C_9H_5N\cdot CO\cdot CH_2\cdot CO_2Et$, which crystallises in almost colourless, matted needles, m. p. 84—85°, gives a *hydrobromide*, yellow crystals, m. p. 159—160°, and yields 6-methoxy-4-quinolyl methyl ketone, m. p. 89—90°, on hydrolysis with 25% sulphuric acid (compare Kaufmann, A., 1912, i, 1017). *Ethyl bromo-6-methoxy-4-quinoloylacetate* is obtained by the action of bromine, diluted with chloroform, on the above hydrobromide. It is pale yellow, has m. p. 81—82°, forms a *hydrobromide*, m. p. 129°, and yields *6-methoxy-4-quinolyl bromomethyl ketone*, $OMe\cdot C_9H_5N\cdot CO\cdot CH_2Br$, on hydrolysis with 24% hydrobromic acid. The free ketone is pale yellow, has m. p. 66—67°, is not very stable, forms a *hydrobromide*, m. p. 197—198°, and can also be prepared by brominating 6-methoxy-4-quinolyl methyl ketone. When the hydrobromide is left with piperidine (3 mols.) diluted with benzene, *6-methoxy-4-quinolyl piperidinomethyl ketone* is formed as an oil, which gives a *hydrobromide*, 1HBr, m. p. 182—185° (decomp.). This ketone, dissolved in concentrated hydrobromic acid, may be reduced by means of hydrogen and palladium-black to *α-6-methoxy-4-quinolyl-β-piperidinoethyl alcohol*, $C_5H_{10}N\cdot CH_2\cdot CH(OH)\cdot C_9H_5N\cdot OMe$, which crystallises in colourless prisms, m. p. 109°.

Ethyl 4-quinoloylacetate (*loc. cit.*) forms a *hydrobromide*, m. p. 162° (decomp.), which can be converted into *ethyl bromo-4-quinoloylacetate*, m. p. 95—96° (*hydrobromide*, brilliant yellow, m. p. 127—128°; *platinichloride*, reddish-yellow, m. p. 122—123°, decomp.), and then into *4-quinolyl bromomethyl ketone*, m. p. 74—75° (*hydrobromide*, lemon-yellow, m. p. 220°, decomp.). This reacts with piperidine to form *4-quinolyl piperidinomethyl ketone*, which is a viscous, yellow oil; *hydrobromide*, B,HBr, m. p. 178° (decomp.); *platinichloride*, B,H_2PtCl_6, m. p. 263° (decomp.); *picrate*, $B,2C_6H_3O_7N_3$, m. p. 133—134° (decomp.).

α-4-Quinolyl-β-piperidinoethyl alcohol, the product of the reduction of the ketone, is also a viscous oil, which forms a pale yellow *platinichloride*, B,H_2PtCl_6, m. p. 232° (decomp.), and a yellowish-green *dipicrate*, m. p. 172—174° (decomp.).

When 4-quinolyl bromomethyl ketone hydrobromide is added to a solution of ethyl cincholeuponate in benzene, dissolution soon takes place, and then *ethyl cincholeuponate hydrobromide*, m. p. 126°, gradually separates, leaving *ethyl 1-4′-quinoloylmethyl-5-ethylpiperidino-4-acetate* in solution, as a viscous mass. The *platinichloride* of this, $C_{22}H_{28}O_3N_2,H_2PtCl_6$, is a yellowish-brown powder, m. p. 197° (decomp.), and the *picrolonate*, $B,2C_{10}H_8O_5N_4$, forms reddish-brown crystals, m. p. 146—147°. The corresponding *secondary alcohol*,

$$CO_2Et\cdot CH_2\cdot CH{<}\begin{matrix}CHEt\cdot CH_2\\ CH_2{-}CH_2\end{matrix}{>}N\cdot CH_2\cdot CH(OH)\cdot C_9H_5N,$$

is also a viscous oil, and its *picrolonate* is reddish-brown.

The "acetoacetic acid" synthesis can be developed a stage

further in this series by treating the sodium compounds of the quinoloylacetic esters with alkyl iodides. Thus, ethyl 4-quinoloylacetate, sodium methoxide, and methyl iodide react to form ethyl α-4-quinoloylpropionate, which has not been purified, but identified by conversion into 4-quinolyl ethyl ketone (*loc. cit.*). J. C. W.

New Method of Preparing Cyclic Ketones. ALFRED SCHAARSCHMIDT (*Ber.*, 1917, **50**, 164—169. Compare A., 1914, i, 732).—Eckert and Halla (A., 1914, i, 994) obtained a compound, which they designated 1 : 2 : 6 : 7-diphthaloylacridone, by condensing 1-aminoanthraquinone-2-carboxylic acid with 2-chloroanthraquinone in the presence of sodium acetate and cuprous chloride. A compound which undoubtedly has this constitution was just previously described by Schaarschmidt (*ibid.*, 732; D.R.-P., 269800), and earlier still in D.R.-P., 192436, but it is not identical with Eckert and Halla's substance. It is suggested that the latter may be a dianthraquinonylamine, for aminoanthraquinonecarboxylic acids tend to lose carbon dioxide on heating (see D.R.-P., 268219; *ibid.*, 184).

The paper deals largely with questions of priority, in which Ullmann and Bincer (A., 1916, i, 483) are concerned. J. C. W.

New Stains for Microscopic Work Derived from Methylene-blue. L. TRIBONDEAU and J. DUBREUIL (*Compt. rend.*, 1917, **164**, 551—553).—An account of a simple method for preparing methylene-violet and methylene-azure in a pure state. To a 1% aqueous solution of methylene-blue 5—10% of ammonia is added and the mixture heated on a water-bath, when an abundant precipitate is formed, which is filtered off. The filtrate is evaporated in a flat dish at 37—40°, the dry residue being methylene-violet. The precipitate on the paper and in the flask is left exposed to the air for a day until it is deep blue in colour. It is then extracted with water, filtered, and the filtrate evaporated as above, the product being methylene-azure. W. G.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. W. MADELUNG (*Ber.*, 1917, **50**, 105—111. Compare Woker, this vol., i, 62).—A criticism of Woker's views on the constitution of the benzidine monohydrochlorides and the oxidation product of benzidine. Attention is re-directed to the author's own communications (A., 1911, i, 323, 411, 678). J. C. W.

Preparation of Ether-like Derivatives of Barbituric Acid. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 295492; from *J. Soc. Chem. Ind.*, 1917, **36**, 306).—Aryl- or alkyl-aryloxyalkylmalonic acids or diaryloxyalkylmalonic acids or their derivatives, for example, the corresponding esters, acid chlorides, cyanoacetates, or malononitriles, are converted into barbituric acid derivatives by the usual methods. Alternatively, mono-substituted malonic acid derivatives containing one of the substituent groups above speci-

fied are converted into barbituric acids and the second substituent group is introduced by alkylation of the resulting mono-substituted barbituric acids or of the product at an intermediate stage of the conversion. Such ether-like derivatives, containing at least one aryl residue attached to an oxygen atom, possess strong hypnotic action combined with low toxic effects. Ethylphenoxyethylbarbituric acid, diphenoxyethylbarbituric acid, *C*-*C*-propyl-*p*-tolyloxyethylbarbituric acid, and *C*-*C*-benzylphenoxyethylbarbituric acid are described. H. W.

[Derivatives of Uric Acid.] HEINRICH BILTZ (*Annalen*, 1916, **413**, 1—7).—An introduction to the following papers. The results of researches by the author and his co-workers in the uric acid series have now accumulated to such an extent that it seems advisable to give a survey of the region traversed, although the investigations are not yet finished. C. S.

Derivatives of Uric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 7—60).—A series of new reactions of uric acid is described.

The glycol ethers of uric acid itself are more difficult to prepare than are those of many methylated uric acids. 4 : 5-*Dimethoxy*-4 : 5-*dihydrouric acid* (*uric acid*-4 : 5-*diglycol dimethyl ether*),

$$\begin{array}{l}NH\cdot CO-C(OMe)\cdot NH \\ CO\cdot NH\cdot C(OMe)\cdot NH\end{array}\!\!>CO,$$

slender needles, m. p. 202—203° (decomp.), is obtained by passing a rapid stream of chlorine into a suspension of uric acid in methyl alcohol, the temperature being kept below 15°; in order to prevent an explosion, the end of the chlorine delivery tube must be about 1 cm. from the bottom of the flask. The corresponding diethyl ether cannot be obtained in a similar manner.

4 : 5-Dimethoxy-4 : 5-dihydrouric acid is reduced to uric acid by sodium amalgam and to ψ-uric acid by hydriodic acid, D 1·96, on the water-bath. When boiled with methyl alcohol saturated with hydrogen chloride, it is converted into a *substance*, $C_6H_8O_5N_2$, stout prisms with domed ends or tufts of stout needles, m. p. 135—137°, which is regarded as *methyl* 5-*methoxyhydantoin*-5-*carboxylate*, $\begin{array}{l}NH-CO \\ CO\cdot NH\end{array}\!\!>C(OMe)\cdot CO_2Me$, since it is easily reduced to hydantoin by concentrated hydriodic acid and phosphonium iodide on the water-bath.

4 : 5-Dimethoxy-4 : 5-dihydrouric acid is converted into alloxantin by 20% hydrochloric acid on the water-bath, but when dissolved in concentrated hydrochloric acid at the ordinary temperature it yields 5 *methoxy*-ψ-*uric acid*, $CO\!<\!\begin{array}{l}NH\cdot CO \\ NH\cdot CO\end{array}\!\!>C(OMe)\cdot NH\cdot CO\cdot NH_2$, stout rhombohedra, m. p. 202—204° (decomp.). The latter is proved to be a derivative of ψ-uric acid by its reduction to ψ-uric acid by sodium amalgam or hydriodic acid and by its formation from ψ-uric acid, methyl alcohol, and chlorine. By boiling with glacial acetic acid for one hour it is converted into 4-*hydroxy*-5-*methoxy*-

4:5-*dihydrouric acid*, stout prisms, m. p. 202—203° (decomp.), which is reduced to hydantoin by hydriodic acid. The conversion of 4:5-dimethoxy-4:5-dihydrouric acid into ψ-uric acid by hydriodic acid is readily explicable in view of the preceding formation of 5-methoxy-ψ-uric acid.

A solution of uric acid in boiling chloroform or in glacial acetic acid is not attacked by chlorine. When, however, water is present in the latter solvent, reaction occurs; with 5 mols. of water the product is alloxan, whilst with 1 mol. of water, the temperature being kept at about 10°, 5-*chloro-ψ-uric acid*,

$$CO{<}\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}{>}CCl\cdot NH\cdot CO\cdot NH_2,$$

is formed. This substance, m. p. about 125° (decomp.), forms very thin, felted fibres or needles containing 1 mol. $C_2H_4O_2$, which cannot be removed. It is also formed by the action of chlorine on ψ-uric acid dissolved in glacial acetic acid. It is reduced to ψ-uric acid by a concentrated solution of hydrogen iodide in glacial acetic acid on the water-bath, by a solution of potassium iodide, iodine being liberated, or by stannous chloride and hydrochloric acid. Since the last method of reduction proceeds very readily, a very convenient method of converting uric acid into ψ-uric acid is presented by chlorinating a solution of uric acid and 1 mol. of water in glacial acetic acid, removing the dissolved chlorine by a current of dry air at 0°, and treating the solution with stannous chloride and concentrated hydrochloric acid.

By treatment with hot methyl alcohol 5-chloro-ψ-uric acid is converted into 5-methoxy-ψ-uric acid. 5-*Ethoxy-ψ-uric acid*, $C_7H_{10}O_5N_4$, forms stout prisms, m. p. 227—228° (decomp.).

Whilst all chloro-ψ-uric acids hitherto known react with water to form the glycols of the corresponding uric acids or their products of decomposition, 5-chloro-ψ-uric acid is unique in yielding 5-*hydroxy-ψ-uric acid*, $C_5H_6O_5N_4$, microscopic leaflets, m. p. about 210° (decomp.), which is converted into alloxan and carbamide by boiling water, yields 4:5-dihydroxy-4:5-dihydrouric acid by slow evaporation with water at 45—50° or by treatment with aqueous bromine at the ordinary temperature, and is reduced to ψ-uric acid by hydriodic acid, D 1·96, sodium amalgam, or acidified aqueous potassium iodide. When boiled with methyl or ethyl alcohol, 5-hydroxy-ψ-uric acid is converted into the corresponding 5-alkyloxy-ψ-uric acid; propyl-, benzyl-, and phenyl-oxy-compounds are not produced in a similar manner, and an acetyl derivative cannot be obtained.

When the basic reagent is added only in slight excess, 5-hydroxy-ψ-uric acid intimately mixed with water reacts with aqueous ammonia at 0° and with 33% methylamine, 33% ethylamine, dimethylamine, diethylamine, and aniline at the ordinary temperature to form the following compounds: 5-*amino-ψ-uric acid*, $C_5H_7O_4N_5,H_2O$, rectangular or quadratic plates, m. p. 145—147° (decomp.); 5-*methylamino-ψ-uric acid*, $C_6H_9O_4N_5$, stout, six-sided or rhombic plates, m. p. 191—192° (decomp.); 5-*ethylamino-ψ-uric*

acid, stout plates, m. p. 170—171° (decomp.); 5-*dimethylamino-ψ-uric acid*, stout needles, m. p. 191—192° (decomp.); 5-*diethylamino-ψ-uric acid*, stout, many-faced crystals (? scalenohedra), m. p. 163—165° (decomp.); and 5-*anilino-ψ-uric acid*, six-sided leaflets, m. p. 194—196° (decomp.).

5-Amino-ψ-uric acid forms an *ammonium* salt, $C_5H_7O_4N_5,NH_3$, elongated, flattened rhombs, m. p. 90—95° (decomp.; reddening at about 70°), and a *hydrochloride*, $C_5H_9O_4N_5,HCl$, microscopic spindles, is reduced to uramil by hydriodic acid, D 1·5, or stannous chloride and hydrochloric acid, and dissolves in 5% aqueous ammonia to yield, after acidification with acetic acid, 5-*amino*-4-*hydroxy*-4 : 5-*dihydrouric acid*, $C_5H_7O_4N_5$, six-sided plates, m. p. 189—191° (decomp.); attempts to effect a similar ring closure in the preceding 5-alkylamino-ψ-uric acids have been unsuccessful.

spiro-5 : 5-*Hydantoin*, $\begin{matrix}NH{-}CO\\ |\qquad\\ CO{\cdot}NH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NH{\cdot}CO\\ \qquad|\\ CO{-}NH\end{matrix}$, stout rhombohedra blackening above 400°, prepared by boiling 5-amino-4-hydroxy-4 : 5-dihydrouric acid with concentrated hydrochloric, nitric, or hydriodic acid, is the parent substance of hypocaffeine (1 : 7 : 9-trimethyl*spiro*-5 : 5-hydantoin) and 1 : 3 : 7 : 9-tetramethyl*spiro*-5 : 5-hydantoin (Biltz and Krebs, A., 1911, i, 240). It is remarkably stable to acids and is not attacked by alkaline permanganate, but is converted into allantoin by hot, concentrated aqueous barium hydroxide and into potassium uroxanate by hot aqueous potassium hydroxide, allantoin-5-carboxylic acid being a probable intermediate product in each case.

The preceding 5-alkylamino- or -dialkylamino-ψ-uric acids are reduced to 7-alkyl- or 7 : 7-dialkyl-uramils by hydriodic acid or stannous chloride and hydrochloric acid. This not only proves the position of the substituted amino-group, but also indicates a very convenient method of preparing substituted uramils, particularly 7 : 7-dimethyluramil. A mixture of pure 5-hydroxy-ψ-uric acid and anhydrous alcohol is shaken vigorously with 33% aqueous methylamine (slightly more than 2 mols.) and the resulting *methylammonium* salt of 5-methylamino-ψ-uric acid, $C_6H_9O_4N_5,NH_2Me$, stout, badly formed crystals, m. p. 110—115° (decomp.), is boiled with a solution of stannous chloride in concentrated hydrochloric acid, whereby 7-methyluramil is obtained after dilution with dilute hydrochloric acid. 7-Ethyluramil is obtained in a similar manner from the *ethylammonium* salt of 5-ethylamino-ψ-uric acid, $C_7H_{11}O_4N_5,NH_2Et$, rectangular plates, decomp. about 140—145°. 7 : 7-*Dimethyluramil*, $C_6H_9O_3N_3,2H_2O$, forms very slender, elongated needles, m. p. 283—285° (decomp.), and in contrast to other uramils is remarkably easily soluble in water.

By reduction with sodium amalgam, 5-amino- and -monoalkylamino-ψ-uric acids yield the corresponding uramils, whilst the 5-dialkylamino-ψ-uric acids yield ψ-uric acid.

Carbamide alloxanate (Behrend and Zieger, A., 1915, i, 165) is obtained by warming a solution of 4 : 5-dihydroxy-4 : 5-dihydrouric acid hemihydrate in water containing a little hydrochloric acid at 60—70°.

After many unsuccessful attempts to convert 4 : 5-dihydroxy-4 : 5-

dihydrouric acid into caffolide, the following simple method yielded the desired product. The glycol is treated with 20% aqueous potassium hydroxide, and the solution after five minutes is acidified with 30% sulphuric acid at 0°, filtered, and repeatedly extracted with ether; the addition of light petroleum to the dried, concentrated ethereal extracts yields *caffolide*, $\begin{matrix}NH\cdot CO\\ | \\ CO—O\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NH\cdot CO\\ | \\ CO—NH\end{matrix}$, tufts of colourless needles, decomp. 220°. Its *disilver* salt, $C_5HO_5N_3Ag_2$, needles, is stable to light, and is converted into *isoapo*caffeine (Biltz, A., 1913, i, 1376) by methyl iodide at 100°.

Although methylated caffolides are easily converted into the corresponding 5-hydroxyhydantoin-5-carboxyamides by boiling and evaporating their aqueous solutions, caffolide itself must be boiled with water and the solution evaporated under increased pressure. 5-*Hydroxyhydantoin*-5-*carboxyamide*, $C_4H_5O_4N_3$, forms rectangular plates, m. p. 191° (decomp.), and yields hydantoin by reduction with hydriodic acid and parabanic acid by oxidation with potassium dichromate and sulphuric acid. C. S.

Preparation of Alloxan. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 60—67).—Finely powdered uric acid is boiled with glacial acetic acid and water (about 5 mols. of the latter), while with continuous, vigorous shaking of the flask a stormy current of chlorine is passed in by a tube reaching almost to the bottom. Towards the end of the reaction the mixture becomes yellowish-green through the presence of dissolved chlorine, and soon after, the uric acid having all dissolved, alloxan monohydrate begins to separate in stout, heavy crystals, the separation being completed by cooling in water at 0°. Unnecessarily prolonged chlorination is to be avoided. The method is recommended as a lecture experiment.

A description is given of the appearance under the microscope of the crystals obtained when the following uric acids (0·03—0·05 gram) are dissolved in concentrated sulphuric acid (about 8 drops) at 40—50° and the clear solutions are stirred into about 5 c.c. of water: uric acid, 1-, 3-, and 7-methyluric acids, 1:3-, 1:7-, 3:9-, and 3:7-dimethyluric acids, 1:3:7-trimethyluric acid, and tetramethyluric acid. C. S.

Alloxanic Acid. HEINRICH BILTZ, MYRON HEYN, and MARGARETE BERGIUS (*Annalen*, 1916, **413**, 68—77).—The constitution $NH_2\cdot CO\cdot NH\cdot CO\cdot CO\cdot CO_2H$ for alloxanic acid appears never to have been proved and never to have been doubted. Several observations recorded in the literature, such as the oxidation by nitric acid of alloxanic acid to parabanic acid by Schlieper, and its reduction by hydriodic acid to hydantoin by Baeyer, not being readily explicable by the open-chain formula, the authors have investigated the subject, and have proved that alloxanic acid is the cyclic compound, 5-hydroxyhydantoin-5-carboxylic acid,

$$\begin{matrix}NH—CO\\ | \\ CO\cdot NH\end{matrix}\!\!>\!C(OH)\cdot CO_2H.$$

It is shown that the oxidation to parabanic acid proceeds quantitatively. According to the new formula, alloxanic acid is dibasic (compare Limpricht, *Annalen*, 1859, **111**, 133), the hydrogen of the carboxyl group and that of the imino-group in position 3 being replaceable by metals. *Methyl alloxanate*, $C_5H_6O_5N_2$, prepared from alloxanic acid and methyl-alcoholic hydrogen chloride in the complete absence of moisture, forms small, pointed, flattened needles, m. p. 171°; the *ethyl* ester has m. p. 115°. When heated with methyl-alcoholic hydrogen chloride at 100°, the methyl ester is converted into methyl 5-methoxyhydantoin-5-carboxylate (Biltz and Heyn, preceding abstract).

Of the two formulæ of alloxanic acid in question, only the open-chain one contains a carbonyl group attached to two carbon atoms. Such carbonyl groups react normally with hydroxylamine, phenylhydrazine, and semicarbazide, whereas a carbonyl group attached to carbon and to nitrogen does not. It is found that alloxan yields precipitates with the three reagents, whereas the alloxanic ester and 3-methylhydantoin do not, the evidence being thus in favour of the cyclic constitution of alloxanic acid. The hydroxyl group in the latter, however, cannot be detected by phenylcarbimide.

Further support of the cyclic structure is given by the formation of *spiro*-5 : 5-hydantoin when a mixture of carbamide and methyl alloxanate or methyl 5-methoxyhydantoin-5-carboxylate is heated at 150° in a current of hydrogen chloride.

The formation of alloxanic acid from alloxan is attributed to a kind of pinacolin transformation:

$$C(OH)_2<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}>CO \longrightarrow CO_2H\cdot C(OH)<\begin{matrix}NH\cdot CO\\ CO-NH\end{matrix}.$$

Piloty and Finckh (A., 1904, i, 824) regard oxonic acid as 5-aminohydantoin-5-carboxylic acid; its formation by the oxidation of uramil is explicable by a transformation of an intermediate oxidation product:

$$NH_2\cdot C(OH)<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}>CO \longrightarrow CO_2H\cdot C(NH_2)<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}.$$

C. S.

*spiro***Hydantoins.** HEINRICH BILTZ, MYRON HEYN, and MARGARETE BERGIUS (*Annalen*, 1916, **413**, 77—87).—Since tetramethyluric acid and 1 : 3 : 7-trimethyluric acid glycol ether are converted respectively into tetramethyl- and trimethyl-*spiro*-5 : 5-hydantoin (A., 1911, i, 240), doubtless by a kind of pinacolin transformation of the intermediate, unstable glycols, which cannot be isolated, it becomes of interest to ascertain whether the more stable uric acid glycols undergo such a transformation. *spiro*-5 : 5-Hydantoin is obtained by heating 4 : 5-dihydroxy-4 : 5-dihydrouric acid with concentrated sulphuric acid on the water-bath, and pouring the cold solution into water. A better yield is obtained by heating the glycol and carbamide at 150° in a current of hydrogen chloride.

The latter is the most convenient method of preparing *spiro*-5 : 5-hydantoin, alloxan being used in place of the uric acid glycol. The 3 : 7-*disilver* salt, $C_5H_2O_4N_4Ag_2,2H_2O$, crystals, obtained by adding a solution of *spiro*-5 : 5-hydantoin in aqueous ammonia to a solution of silver nitrate, is converted by methyl iodide and a little dry silver oxide at 100° into 3 : 7-*dimethyl*spiro-5 : 5-*hydantoin* (annexed formula for numbering), small prisms, m. p. 297—298°, the constitution of which is determined, not only by the fact that in the generating disilver salt the metallic atoms must have replaced the acidic hydrogen atoms of the imino-groups between each pair of carbonyl groups in *spiro*-5 : 5-hydantoin, but also by its conversion in aqueous solution by basic lead acetate on the water-bath into 3 : 8-*dimethylallantoin*,

$$\begin{array}{l}\overset{3}{N}Me{\cdot}\overset{4}{CO} \\ \underset{2}{C}O{-}{-}\underset{1}{N}H\end{array}\!\!>\overset{5}{C}<\!\!\begin{array}{l}\overset{9}{N}H{\cdot}\overset{8}{C}O \\ \underset{6}{C}O{-}{-}\underset{7}{N}Me\end{array}$$

$$\begin{array}{l}NMe{\cdot}CO \\ CO{-}{-}NH\end{array}\!\!>CH{\cdot}NH{\cdot}CO{\cdot}NHMe,$$

stout, indistinctly formed prisms, m. p. 222° (decomp.), from which 3-methylhydantoin is obtained by reduction with hydriodic acid.

4 : 5-Dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid is converted by concentrated sulphuric acid on the water-bath into 1 : 9-*dimethyl*spiro-5 : 5-*hydantoin*, $\begin{array}{l}NH{-}CO \\ CO{\cdot}NMe\end{array}\!\!>C<\!\!\begin{array}{l}NMeCO \\ CO{-}{-}NH\end{array}$, small, four-sided pointed prisms, m. p. 264—265°, which yields 1 : 6-*dimethylallantoin*, $C_6H_{10}O_3N_4$, flat, pointed needles, m. p. 226—227° (decomp.), by treatment with basic lead acetate, forms the *disilver* salt, $C_7H_6O_4N_4Ag_2$, and is converted into tetramethyl-*spiro*-5 : 5-hydantoin by shaking with methyl sulphate and aqueous sodium hydroxide. 1 : 6-Dimethylallantoin is converted into 1-methylhydantoin by reduction with hydriodic acid.

The glycols of 9-methyluric acid and 1 : 3-dimethyluric acid could not be converted into *spiro*hydantoins. C. S.

Derivatives of 9-Methyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 87—98).—9-Methyluric acid has hitherto been obtained only with difficulty. The authors prepare it easily from 5-chloro-9-methyl-ψ-uric acid, which is itself obtained as follows. The crude methyluric acid (or mixture), prepared by acidifying the hot solution obtained by heating uric acid, dilute aqueous potassium hydroxide, and methyl iodide in a closed bottle in a water-bath, is finely powdered, mixed with glacial acetic acid, and treated at 0° with a vigorous stream of chlorine, the temperature being kept below 10°. 5-*Chloro*-9-*methyl*-ψ-*uric acid*, $CO<\!\!\begin{array}{l}NH{\cdot}CO \\ NH{\cdot}CO\end{array}\!\!>CCl{\cdot}NH{\cdot}CO{\cdot}NHMe$, leaflets, containing $\frac{1}{2}C_2H_4O_2$, m. p. 208—210° (decomp.), thus obtained, is converted into 4 : 5-dihydroxy-9-methyl-4 : 5-dihydrouric acid by luke-warm water, and into 5-*methoxy*-9-*methyl*-ψ-*uric acid*, $C_7H_{10}O_5N_4$, octagonal or quadratic plates, m. p. 195—196° (decomp.), and

5-*ethoxy*-9-*methyl*-ψ-*uric acid*, colourless needles, m. p. 222° (decomp.), by rubbing with methyl and ethyl alcohol respectively. By crystallisation from water, the last two compounds are converted into 4-*hydroxy*-5-*methoxy*-9-*methyl*-4 : 5-*dihydrouric acid*, $C_7H_{10}O_5N_4$, cubes or rhombohedra, m. p. 170—172° (which yields 3-methylhydantoin by reduction with hydriodic acid), and 4-*hydroxy*-5-*ethoxy*-9-*methyl*-4 : 5-*dihydrouric acid*, thin leaflets, m. p. 190—192°.

9-*Methyl*-ψ-*uric acid*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot NH\cdot CO\cdot NHMe$, m. p. 260—261° (decomp.), needles or prisms containing $1H_2O$, is obtained by reducing 5-chloro-9-methyl-ψ-uric acid with stannous chloride and concentrated hydrochloric acid, or the 5-alkyloxy-9-methyl-ψ-uric acids at 40—50° with a saturated solution of hydrogen iodide in glacial acetic acid. It is converted by prolonged evaporation with 20% hydrochloric acid into 9-methyluric acid, the identity of which was proved by its m. p., very sparing solubility in boiling water (1 part in 1830), and conversion into 1-methylallantoin, alloxantin, and dialuric acid. By treatment with chlorine, 9-methyluric acid dissolved in glacial acetic acid and a little water is converted into 5-chloro-9-methyl-ψ-uric acid, and from the yield obtained it was calculated that the original crude mixture contained 20—30% of 9-methyluric acid. C. S.

α-, ζ- **and** δ-**Methyluric Acids.** HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 98—124).—The authors have solved the mystery of the three isomeric methyluric acids, for which only one formula is available, namely, Hill's α-methyluric acid, von Loeben's δ-methyluric acid, and Fischer and Ach's ζ-methyluric acid, in all of which, so far as our knowledge goes, the methyl group is in position 3.

α-Methyluric acid was prepared according to Grohmann's directions (A., 1911, i, 691), and purified through the sodium salt in order to remove unchanged uric acid, none of which, however, was found to be present (compare Grohmann, *loc. cit.*). In the purification, about one-half of the sodium salt separates as a solid and the other half remains in solution. The α-methyluric acids obtained from these two portions were separately treated with chlorine and glacial acetic acid (compare preceding abstract), and from the amounts of 5-chloro-9-methyl-ψ-uric acid obtained it was calculated that the α-methyluric acid obtained from the precipitated sodium salt contained about 20%, and that from the soluble sodium salt about 32%, of 9-methyluric acid. By the same method of analysis, the crude α-methyluric acid (not purified through the sodium salt) was estimated to contain about 25% of 9-methyluric acid, and this estimate could be, and was, confirmed by the amount of the water of crystallisation, since 9-methyluric acid crystallises anhydrous and 3-methyluric acid with $1H_2O$.

ζ-Methyluric acid, prepared by Fischer and Ach's method, was examined in the same way, and according to the amount of 5-chloro-

9-methyl-ψ-uric acid obtained was estimated to contain about 10% of 9-methyluric acid.

δ-Methyluric acid synthesised by von Loeben's method cannot contain 9-methyluric acid, and therefore did not yield any 5-chloro-9-methyl-ψ-uric acid. This is the true 3-methyluric acid; the α- and the ζ-acids contain, in addition, 25% and 10% respectively of 9-methyluric acid. The presence of 3-methyluric acid in the α- and ζ-acids is proved not only by their conversion into methylalloxan and 1-methylallantoin by oxidation, and into chloro-3-methylxanthine by phosphoryl chloride at 140—150°, but also in the following new way. By chlorination in dry chloroform, 3-methyluric acid yields a very hygroscopic chlorination product, probably the 4:5-dichloride, which is converted by methyl alcohol into 4-*hydroxy*-5-*methoxy*-3-*methyl*-4:5-*dihydrouric acid*, $C_7H_{10}O_5N_4$, monoclinic prisms [$a:b:c=0·86806:1:0·67908$; $\beta=56°8'$], m. p. 207° (decomp.). This substance was obtained from α- and from ζ-methyluric acid, thus proving the presence of 3-methyluric acid in these two acids.

The records state that 1 part of δ-methyluric acid dissolves in 527 parts of boiling water (von Loeben), 1 part of α-methyluric acid in 262 parts (*ibid.*), 1 part of ζ-methyluric acid in about 600, and 1 part of 9-methyluric acid in more than 2000 (Fischer and Ach). These results being peculiar, in view of the compositions ascribed above to the first three acids, the authors have redetermined the solubilities of all the acids in boiling water under the same conditions, and find that mixtures of 9- and 3-methyluric acids are indeed more soluble than either of the constituents. The amount of boiling water required to dissolve 1 part of the acid is: 9-methyluric acid, 1830; 3-methyluric acid, 630; 90% of 3- and 10% of 9-methyluric acids, 360; 70% of 3- and 30% of 9-methyluric acids, 270; ζ-methyluric acid, 475; and α-methyluric acid, 200. The mixtures do not appear to dissolve as isomorphous mixed crystals, but leave a solid phase (or phases) differing in composition and solubility from the portion in solution, so that variable values of the solubility of a given mixture are obtained according to the relative proportions of mixture and water. Uric acid requires 1250 parts, and 3:7-dimethyluric acid 290 parts, of boiling water for solution. All these measurements profess to give only the orders of magnitude, not the accurate values, of the solubility. 7-Methyluric acid exhibits an extraordinary tendency to form supersaturated solutions. C. S.

Derivatives of 1-Methyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1916, **413**, 124—136).—4:5-*Dimethoxy*-1-*methyl*-4:5-*dihydrouric acid*, $\begin{matrix}\text{NMe·CO·C(OMe)·NH}\\ \text{CO–HN–C(OMe)·NH}\end{matrix}\!\!>\!\text{CO}$, six-sided plates, m. p. 225° (decomp.), is obtained by passing a rapid stream of chlorine into a mixture of finely powdered 1-methyluric acid and glacial acetic acid at 0°. The corresponding 4:5-*diethoxy*-compound forms slender needles, m. p. 212° (decomp.). In

both cases a small amount of the 5-alkyloxy-1-methyl-ψ-uric acid is obtained as a by-product. 5-*Methoxy*-1-*methyl-ψ-uric acid*, $CO<\substack{NMe\cdot CO \\ NH-CO}>C(OMe)\cdot NH\cdot CO\cdot NH_2$, rectangular leaflets, m. p. about 192° (decomp.), is obtained (1) when 4 : 5-dimethoxy-1-methyl-4 : 5-dihydrouric acid is triturated with concentrated hydrochloric acid or boiled with alcoholic hydrochloric acid, (2) by chlorinating a mixture of 1-methyluric acid or 1-methyl-ψ-uric acid and methyl alcohol at the ordinary temperature. 5-*Ethoxy*-1-*methyl-ψ-uric acid*, obtained by similar methods, forms leaflets, m. p. about 216° (decomp.).

4 : 5-Dimethoxy-1-methyl-4 : 5-dihydrouric acid is reduced to 1-methyluric acid by $2\frac{1}{2}$% sodium amalgam or by hydriodic acid, D 1·96, on the water-bath, but when hydriodic acid, D 1·5, is used at 60° the product is 1-methyl-ψ-uric acid, which is also obtained in a similar way from 5-methoxy-1-methyl-ψ-uric acid.

5-*Chloro*-1-*methyl-ψ-uric acid*,

$$CO<\substack{NMe\cdot CO \\ NH-CO}>CCl\cdot NH\cdot CO\cdot NH_2,$$

indistinct crystals containing $1C_2H_4O_2$, m. p. about 170° (decomp.), is obtained by chlorinating 1-methyluric acid or 1-methyl-ψ-uric acid in the presence of glacial acetic acid. It is converted into 5-methoxy-1-methyl-ψ-uric acid by gently warming with methyl alcohol containing a few drops of glacial acetic acid, yields 1-methyl-ψ-uric acid by heating with glacial acetic acid saturated with hydrogen iodide, and reacts with water to form 4 : 5-*dihydroxy*-1-*methyl*-4 : 5-*dihydrouric acid*, $C_6H_8O_5N_4$, elongated leaflets, m. p. 140° (decomp.).

When 5-methoxy-1-methyl-ψ-uric acid is dissolved in 4*N*-sodium hydroxide and the solution is acidified with concentrated hydrochloric acid, a substance is obtained which is identical with the 4-hydroxy-5-methoxy-3-methyl-4 : 5-dihydrouric acid prepared by Biltz and Heyn (preceding abstract) from 3-methyluric acid. It is evident that when 5-methoxy-1-methyl-ψ-uric acid undergoes isomerisation, the formation of the glyoxaline ring may result by the union of the carbamido-group with either of the contiguous carbonyl groups. It has not yet been definitely ascertained in which direction the union occurs, so the product of isomerisation may be either 4-hydroxy-5-methoxy-1-methyl-4 : 5-dihydrouric acid or 4-hydroxy-5-methoxy-3-methyl-4 : 5-dihydrouric acid, but the latter is the more probable in view of the evidence obtained by Biltz and Damm (following abstract). 4-*Hydroxy*-5-*ethoxy*-3(?)-*methyl*-4 : 5-*dihydrouric acid*, obtained by the isomerisation of 5-ethoxy-1-methyl-ψ-uric acid, forms stout prisms, m. p. 203° (decomp.). C. S.

Derivatives of 1 : 7-Dimethyluric Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1916, **413**, 137—155).—5-*Chloro*-1 : 7-*dimethyl*-$\Delta^{4(9)}$-*isouric acid*, $\begin{matrix} NMe\cdot CO\cdot CCl\cdot NMe \\ | \qquad\qquad | \\ CO\cdot NH-C\!=\!\!=\!\!=\!N \end{matrix}>CO$, obtained by leading chlorine into a mixture of 1 : 7-dimethyluric acid and dry chloroform, has m. p. 131° (decomp.), yields 1 : 7-dimethyluric acid by reduction with hydriodic acid, is converted into *apo*caffeine by

water, and reacts with methyl and ethyl alcohols to form the glycol ethers; 4 : 5-*dimethoxy*-1 : 7-*dimethyl*-4 : 5-*dihydrouric acid*,

$C_9H_{14}O_5N_4$,

four-sided prisms, m. p. 171°, and the 4 : 5-*diethoxy*-compound, $C_{11}H_{18}O_5N_4$, elongated rhombohedra, m. p. 188—189°, which can also be obtained directly from 1 : 7-dimethyluric acid and the alcohol by means of chlorine. These glycol ethers are reduced to 1 : 7-dimethyluric acid by hydriodic acid or sodium amalgam, and react with concentrated hydrochloric or sulphuric acid in an interesting manner. The product should be the 4-hydroxy-5-alkyloxy-1 : 7-dimethyl-4 : 5-dihydrouric acid by analogy with the behaviour of the glycol ethers of the 3 : 7-dimethyluric acid series (Biltz and Damm, A., 1914, i, 1093) or the 5-alkyloxy-1 : 7-dimethyl-ψ-uric acid according to the experience of Biltz and Heyn (preceding abstract). It proves to be neither of these, but to be identical with the 4-hydroxy-5-alkyloxy-3 : 7-dimethyl-4 : 5-dihydrouric acid obtained by Biltz and Damm (*loc. cit.*). This identity would be easily explicable if the substance could be regarded as being actually 5-alkyloxydimethyl-ψ-uric acids, because it is quite clear that the same product must be obtained from 4 : 5-dialkyloxy-1 : 7-dimethyl- and -3 : 7-dimethyl-4 : 5-dihydrouric acids. This view, however, is quite untenable for several reasons: (1) the substances are much too stable to be ψ-uric acid; (2) they cannot be reduced to dimethyl-ψ-uric acid by any means, but yield 1-methylhydantoin, so that they must be nearly related to the 3 : 7-dimethyluric acid glycol, which also yields 1-methylhydantoin; and (3) they yield 3 : 7-dimethyluric acid glycol by hydrolysis. The formation of 4-hydroxy-5-alkyloxy-3 : 7-dimethyl-4 : 5-dihydrouric acid from 4 : 5-dialkyloxy-1 : 7-dimethyl-4 : 5-dihydrouric acid by hydrochloric acid is, therefore, not a simple hydrolysis of the alkyloxy-group in position 4, but is due to the fission of the ether to 5-alkyloxydimethyl-ψ-uric acid, this unstable substance then undergoing isomerisation, the glyoxaline ring being reformed in such a way that 4-hydroxy-5-alkyloxy-3 : 7-dimethyl-4 : 5-dihydrouric acid is produced. The correctness of this view has been proved by the synthesis of the 5-alkyloxydimethyl-ψ-uric acid and its actual conversion into the last-mentioned compound. 5-*Chloro*-1 : 7-*dimethyl*-ψ-*uric acid*,

$$CO{<}\genfrac{}{}{0pt}{}{NMe\cdot CO}{NH—CO}{>}CCl\cdot NMe\cdot CO\cdot NH_2,$$

m. p. 222—223° (decomp.; reddening at about 80°), obtained by passing chlorine into a mixture of dry chloroform and 1 : 7-dimethyl-ψ-uric acid, is reduced to 1 : 7-dimethyl-ψ-uric acid by hydrogen iodide in glacial acetic acid at the ordinary temperature and to 1 : 7-dimethyluric acid by hydriodic acid on the water-bath, and reacts smoothly with methyl alcohol in the presence of pyridine to form 5-*methoxy*-1 : 7-*dimethyl*-ψ-*uric acid*, $C_8H_{12}O_5N_4$, microscopic leaflets, which by rapid heating reddens at about 80—90° and has m. p. 173—174° (decomp.), but when slowly heated softens at about 170°, becomes hard again at about 180°, and then has m. p. 230—240° owing to its conversion into 4-hydroxy-5-methoxy-3 : 7-dimethyl-4 : 5-dihydrouric acid. The same change is effected by

crystallising the substance from water. The preceding hemi-ether is obtained directly from 5-chloro-1 : 7-dimethyl-ψ-uric acid and methyl alcohol in the absence of pyridine, and also by passing chlorine into a mixture of 1 : 7-dimethyl-ψ-uric acid and methyl alcohol at 0°. C. S.

Derivatives of 1 : 3-Dimethyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1916, **413**, 155—179).—In view of the results obtained in the case of 1 : 7-dimethyluric acid (Biltz and Damm, preceding abstract), it becomes of interest to examine the behaviour of 1 : 3-dimethyluric acid and its derivatives under similar conditions. Observations already recorded show that the action of chlorine on uric acids in certain solvents, such as chloroform or glacial acetic acid, produces 5-chloro*iso*uric acids or 5-chloro-ψ-uric acids, the former being usually obtained when the uric acid is alkylated in position 7, for example, 1 : 3 : 7-trimethyluric acid (Biltz, A., 1911, i, 168), 3 : 7-dimethyluric acid (Biltz and Damm, A., 1914, i, 1093), and 1 : 7-dimethyluric acid (*ibid.*, preceding abstract) whilst uric acid itself, 1-methyluric acid, and 9-methyluric acid yield 5-chloro-ψ-uric acids. It is now found that 1 : 3-dimethyluric acid behaves in accordance with this rule, but the chloro*iso*uric acid has also been obtained by a peculiar reaction.

5-*Chloro*-1 : 3-*dimethyl*-$\Delta^{4(9)}$-iso*uric acid*,

$$\left.\begin{array}{l}\text{NMe·CO—CCl·NH}\\ \text{CO·NMe·C}\!=\!\!=\!\!=\!\text{N}\end{array}\right\rangle\text{CO},$$

narrow leaflets, m. p. 225° (decomp.), is obtained by passing chlorine into a well-dried solution of anhydrous theophylline in glacial acetic acid at the ordinary temperature, a particle of iodine being added to act as a catalyst. It resembles other chloro*iso*uric acids in its properties. It is very hygroscopic, is reduced to 1 : 3-dimethyluric acid by hydriodic acid, D 1·96, on the water-bath, or, better, by a saturated solution of hydrogen iodide in glacial acetic acid, is converted into 4 : 5-dihydroxy-1 : 3-dimethyl-4 : 5-dihydrouric acid by water, and reacts with methyl and ethyl alcohols to form 4 : 5-*dimethoxy*-1 : 3-*dimethyl*-4 : 5-*dihydrouric acid*, $C_9H_{14}O_5N_4$, six-sided leaflets, m. p. about 200°, and the corresponding 4 : 5-*diethoxy-compound*, $C_{11}H_{18}O_5N_4$, leaflets, m. p. about 163—165°. These ethers, which can also be prepared by the action of chlorine on a mixture of 1 : 3-dimethyluric acid and the requisite alcohol at 0°, lose 1 mol. of the alcohol by heating at 150—160°/15—20 mm., and are thereby converted into 5-*methoxy*-1 : 3-*dimethyl*-$\Delta^{4(9)}$-iso*uric acid*, $C_8H_{10}O_4N_4$, elongated, pointed leaflets, m. p. 207°, and the corresponding 5-*ethoxy*-compound, irregular prisms, m. p. 195°. These two substances, which are also obtained from 5-chloro-1 : 3-dimethyl*iso*uric acid and the alcohols in the presence of pyridine, are converted into the 4 : 5-dialkyloxy-1 : 3-dimethyl-4 : 5-dihydrouric acids by methyl and ethyl alcohol containing hydrogen chloride.

The 4 : 5-dialkyloxy-1 : 3-dimethyl-4 : 5-dihydrouric acids are reduced to 1 : 3-dimethyluric acid by sodium amalgam or by hydriodic acid, D 1·96, on the water-bath, and to 1 : 3-dimethyl-ψ-uric acid by

hydriodic acid, D 1·5, at about 60°. When warmed with 5% hydrochloric acid or dissolved in concentrated hydrochloric acid at the ordinary temperature they suffer hydrolysis of the alkyloxy-group in position 4 and fission of the glyoxaline ring, yielding thereby 5-*methoxy*-1 : 3-*dimethyl-ψ-uric acid*,

$$CO{<}{\substack{NMe\cdot CO\\ NMe\cdot CO}}{>}C(OMe)\cdot NH\cdot CO\cdot NH_2,$$

stout rhombohedra, m. p. about 186° (decomp.), and the corresponding 5-*ethoxy*-compound, $C_9H_{14}O_5N_4$, felted needles, m. p. 180° (decomp.). These two substances, which can also be obtained (i) by the action of chlorine on a mixture of 1 : 3-dimethyluric acid and the alcohol without cooling, (2) in a similar way from 1 : 3-dimethyl-ψ-uric acid, and (3) from 5-chloro-1 : 3-dimethyl-ψ-uric acid (see below), are proved to be derivatives of ψ-uric acid by the reddening and decomposition accompanying their fusion, by their formation by method (2) above, and by their reduction to 1 : 3-dimethyl-ψ-uric acid by sodium amalgam or hydriodic acid. 5-Methoxy-1 : 3-dimethyl-ψ-uric acid has also been obtained by warming 5-chloro-1 : 3-dimethyl*iso*uric acid with methyl alcohol and keeping the solution overnight in a closed flask, the 4 : 5-dimethoxy-1 : 3-dimethyl-4 : 5-dihydrouric acid initially formed (see above) doubtless reacting with the hydrogen chloride generated to form the final product. 5-n-*Propoxy*-1 : 3-*dimethyl-ψ-uric acid*, $C_{10}H_{16}O_5N_4$, elongated, pointed leaflets, m. p. 177° (decomp.), which slowly separates from a solution obtained by triturating 5-chloro-1 : 3-dimethyl*iso*uric acid with propyl alcohol, doubtless owes its formation to a similar cause.

5-*Chloro*-1 : 3-*dimethyl-ψ-uric acid*, $C_7H_9O_4N_4Cl$, small rhombohedra, m. p. 140° (decomp.), is obtained by the action of chlorine on a mixture of 1 : 3-dimethyluric acid or 1 : 3-dimethyl-ψ-uric acid and glacial acetic acid. It is unique among the chloro-ψ-uric acids in crystallising without acetic acid of crystallisation. It is converted into 4 : 5-dihydroxy-1 : 3-dimethyl-4 : 5-dihydrouric acid (Biltz and Strufe, A., 1914, i, 586) by water; into the 5-alkyloxy-1 : 3-dimethyl-ψ-uric acid by warming with methyl or ethyl alcohol containing a little glacial acetic acid, and into 1 : 3-dimethyl-ψ-uric acid by reduction with hydrogen iodide in glacial acetic acid on the water-bath.

By dissolving 5-methoxy- or 5-ethoxy-1 : 3-dimethyl-ψ-uric acid in 4*N*-sodium hydroxide and acidifying the solution with concentrated hydrochloric acid, 4-*hydroxy*-5-*methoxy*-1 : 3-*dimethyl*-4 : 5-*dihydrouric acid*, $C_8H_{12}O_5N_4,H_2O$, prisms, m. p. 241° (decomp.), and the corresponding 4-*hydroxy*-5-*ethoxy*-compound, prisms, m. p. 244° (decomp.), are obtained. These substances, the latter of which is also obtained, together with 1 : 3-dimethyl-ψ-uric acid, by the reduction of 5-ethoxy-1 : 3-dimethyl-ψ-uric acid by sodium amalgam, are remarkably stable. They can be sublimed without decomposition under reduced pressure, are not attacked by concentrated nitric acid on the water-bath or by a saturated solution of hydrogen iodide in glacial acetic acid at 130°, but are converted by hydriodic acid, (D 1·96), at 130° into a *substance*, $C_5H_7O_3N_3$, leaflets, m. p. 257°

(decomp.), which has not been identified; they are oxidised to dimethylparabanic acid by boiling dilute sulphuric acid and potassium dichromate. C. S.

Derivatives of 1 : 3 : 7-Trimethyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1916, **413**, 179—185).—4 : 5-Dimethoxy-1 : 3 : 7-trimethyl-4 : 5-dihydrouric acid, first prepared by Fischer in 1882, is quite readily obtained, in 85% yield, by the vigorous action of chlorine on a mixture of finely powdered caffeine and methyl alcohol below 20°. The diethoxy-compound cannot be prepared in a similar manner. Both substances are reduced to 1 : 3 : 7-trimethyluric acid by sodium amalgam or by hydriodic acid under various conditions, attempts to isolate 1 : 3 : 7-trimethyl-ψ-uric acid being unsuccessful.

4 : 5-Dimethoxy-1 : 3 : 7-trimethyl-4 : 5-dihydrouric acid is converted by aqueous hydrogen chloride (saturated at 0°) at 0° into 5-*methoxy*-1 : 3 : 7-*trimethyl-ψ-uric acid*, $C_9H_{14}O_5N_4$, pyramidal prisms, m. p. 189—191° (decomp.), the filtrate depositing a small quantity of *apo*caffeine after long keeping; the latter becomes the main product of the reaction when ordinary concentrated hydrochloric acid is used. 5-Methoxy-1 : 3 : 7-trimethyl-ψ-uric acid, which has also been prepared by the action of chlorine on a mixture of 1 : 3 : 7-trimethyl-ψ-uric acid and methyl alcohol, is converted into *apo*caffeine by concentrated sulphuric acid, and is reduced to 1 : 3 : 7-trimethyl-ψ-uric acid by sodium amalgam.

Attempts to prepare 5-chloro-1 : 3 : 7-trimethyl-ψ-uric acid by the action of chlorine on a mixture of 1 : 3 : 7-trimethyluric acid and glacial acetic acid containing 1 mol. of water yielded only 5-chloro-1 : 3 : 7-trimethyl*iso*uric acid (Biltz, A., 1911, i, 168). C. S.

Derivatives of 3 : 7 : 9-Trimethyluric Acid. HEINRICH BILTZ and PAUL DAMM (*Annalen*, 1916, **413**, 186—197).—3 : 7-Dimethyluric acid and theobromine are converted into 1 : 3 : 7-trimethyluric acid and caffeine respectively by shaking with aqueous sodium hydroxide and methyl sulphate. Under similar conditions, 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid, 4-hydroxy-5-methoxy- and -5-ethoxy-3 : 7-dimethyl-4 : 5-dihydrouric acids, and 4-hydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid (Biltz and Damm, A., 1914, i, 1094) are also methylated, but in these four cases the new methyl group enters into position 9. The proof of this in the case of the first of the four substances is given by the fact that the product, 4 : 5-*dihydroxy*-3 : 7 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, $C_8H_{12}O_5N_4$, stout rhombohedra, m. p. 200—201° (decomp.), is also obtained by the action of chlorine on a mixture of 3 : 7 : 9-trimethyluric acid and water at 80°; this substance has also been obtained in the case of the other three products, which therefore also contain the new methyl group in position 9.

4 : 5-Dihydroxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid is a strikingly stable substance, and therefore differs in this respect from 4 : 5-dihydroxy-1 : 3 : 7-trimethyl-4 : 5-dihydrouric acid, which is so

unstable that it has not been isolated, reactions intended to produce it yielding instead its degradation product, *apo*caffeine (Biltz and Krebs, A., 1910, i, 523). The stability of the glycol obtained by methylating 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid is therefore an indirect proof of its constitution, because the new methyl group cannot be in position 1 (in which case the product must be the unstable 1 : 3 : 7-trimethyluric acid glycol), and therefore by exclusion must be in position 9. A second indirect proof of its constitution is furnished by the conversion of 4 : 5-dihydroxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid into *allo*caffeine by prolonged heating with glacial acetic acid on the water-bath; this is explained by the rupture of the glycol into monomethylalloxan and *s*-dimethylcarbamide, these then reacting to give *allo*caffeine (Biltz, A., 1910, i, 522).

4-Hydroxy-5-ethoxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid, $C_{10}H_{16}O_5N_4$, long prisms, m. p. 175°, is obtained by methylation, as stated above, and also by the action of chlorine on a mixture of 3 : 7 : 9-trimethyluric acid and anhydrous ethyl alcohol; it yields 1 : 3-dimethylparabanic acid by oxidation with sulphuric acid and potassium dichromate, and 4 : 5-dihydroxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid by hydrolysis with concentrated sulphuric acid and a few drops of water. *4-Hydroxy-5-methoxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid*, $C_9H_{14}O_5N_4$, plates, m. p. 185°, is obtained by the same two methods as the homologous ethoxy-compound, and also yields 4 : 5-dihydroxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid by hydrolysis.

4-Hydroxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid, small rhombohedra, m. p. 196—197°, prepared by methylation as stated above, is converted into 4-hydroxy-5-ethoxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid and the corresponding 4 : 5-dihydroxy-compound respectively by the action of chlorine on its mixture with ethyl alcohol and on its solution in water.

Attempts to prepare 5-chloro-3 : 7 : 9-trimethyl-ψ-uric acid or 4 : 5-dichloro-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid by the action of chlorine on a mixture of 3 : 7 : 9-trimethyluric acid and chloroform or glacial acetic acid have been unsuccessful, the only product isolated being *allo*caffeine. C. S.

Derivatives of 1 : 3 : 7 : 9-Tetramethyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1916, **413**, 197—206).—It has been observed that the number of derivatives obtainable from the trimethyluric acids by the author's methods is much smaller than in the cases of the di- and mono-methyluric acids and uric acid itself. This is partly due to the greater solubility of the expected products, but still more so to their greater reactivity, in consequence of which they change into stable degradation products. In the case of tetramethyluric acid, only two derivatives have been obtained, apart from *allo*caffeine and 1 : 3 : 7 : 9-tetramethyl-5 : 5-*spiro*hydantoin, which are already known.

1 : 3 : 7 : 9-Tetramethyluric acid can be conveniently prepared in good yield and in large quantities from caffeine by Wislicenus and

Körber's method (1902). By treating a mixture of the acid and methyl alcohol with chlorine at the ordinary temperature, 4:5-*dimethoxy*-1:3:7:9-*tetramethyl*-4:5-*dihydrouric acid*,

$$C_{11}H_{18}O_5N_4,$$

stout prisms, m. p. 133°, is obtained, which is reduced to tetramethyluric acid by hydrogen iodide in glacial acetic acid on the water-bath, and is converted into *allo*caffeine by boiling dilute hydrochloric acid, by hydrochloric acid saturated at 0°, or by alcoholic hydrogen chloride, the hemi-ether, the glycol, or 5-methoxytetramethyl-ψ-uric acid not being produced. 4:5-Diethoxy-1:3:7:9-tetramethyl-4:5-dihydrouric acid cannot be prepared by the action of chlorine on a mixture of tetramethyluric acid and ethyl alcohol; at the ordinary temperature the product is *allo*caffeine, whilst at 0° or in a freezing mixture of ice and sodium chloride, 5-*ethoxytetramethyl-ψ-uric acid*, $C_{11}H_{18}O_5N_4$, leaflets, m. p. 215° (decomp.), together with a little *allo*caffeine, is obtained. The ethoxytetramethyl-ψ-uric acid is converted into *allo*caffeine by boiling dilute hydrochloric acid, and is reduced to tetramethyluric acid by hydriodic acid, D 1·96 or 1·5, on the water-bath, and to *allo*caffeine by hydrogen iodide in glacial acetic acid with cooling by water. C. S.

Acyl Derivatives of Paradiazoiminobenzene. GILBERT T. MORGAN and ADOLPH WILLIAM HENRY UPTON (T., 1917, **111**, 187—196).—In extension of the earlier work on the formation of *p*-diazoimides from various substitution derivatives of *p*-phenylenediamine (T., 1910, **97**, 48; 1908, **93**, 614; 1907, **91**, 1505, etc.), it has now been discovered that formyl-*p*-phenylenediamine and its homologues can be converted into p-diazoimides by diazotising with liquid nitrogen trioxide in acetone. In this manner, there have been obtained *formyl*-p-*phenylenediazoimide*, $\begin{matrix}N_2\\ |\\ C_6H_4\end{matrix}\!\!>\!N{\cdot}COH$, *acetyl*-p-*phenylenediazoimide*, *benzoyl*-p-*phenylenediazoimide*, and *benzoyl*-1:4-*naphthylenediazoimide*, $C_{10}H_6\!<\!\begin{matrix}NBz\\ |\\ N_2\end{matrix}$ The substances of higher molecular weight are more stable than their lower analogues; all are able to couple with β-naphthol, with formation of an azo-compound.

For experimental details see the original. D. F. T.

The Bisulphite Compounds of Azo-colouring Matters. N. N. VOROSHCOV (*Ann. Chim.*, 1916, [ix], **6**, 381—403; 1917, [ix], **7**, 50—113).—A full account of work already published (compare A., 1916, i, 293). W. G.

The Chemistry of the Proteins. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, **78**, 349—353).—When serum is dried in a film on a glass plate, a product is obtained which is soluble in water. If, however, the product is ground up in a mortar, a powder is formed which is no longer completely soluble.

The following explanation is offered of this "mechanical denaturisation" of the protein. The scale preparation is considered to consist of spheres of the protein surrounded by a layer of protein degradation products, to the presence of which the disaggregation of the protein in water is due. By grinding in a mortar, the spheres are broken up, and fresh surfaces are exposed on which there are no degradation products, and owing to the exposure of surfaces of protein without these products, complete solubility is no longer possible. S. B. S.

Behaviour of Casein toward Dilute Solutions of Sodium Chloride. SIGFRID RYD (*Zeitsch. Elektrochem.*, 1913, **23**, 19—23).—After a short discussion on the behaviour of casein toward acids bases and salts generally, and a discussion of the amphoteric character of this substance, the author describes a number of experiments made to determine the solubility of casein in dilute solutions of sodium chloride at 18—20°. A weighed quantity of casein was placed in a measured quantity of sodium hydroxide solution and stirred rapidly until all had dissolved. Then from a burette sufficient hydrochloric acid was added to neutralise the whole of the sodium hydroxide. This precipitated the major portion of the casein, and formed sodium chloride. Then, by the cautious addition of dilute sodium hydroxide and hydrochloric acid, a point was reached at which the addition of a further drop of hydrochloric acid would just produce an opalescence. When this was the case, the solution was saturated with casein. It is shown that the solubility reaches a maximum in sodium chloride solution of 0·1114*N*, and then decreases. J. F. S.

Achroodextrinase. J. EFFRONT (*Compt. rend.*, 1917, **164**, 415—416).—Certain species of *Bacillus mesentericus*, grown in a nitrogenous medium, secrete a diastase which liquefies starch. The author has isolated this diastase, which he calls *achroodextrinase*, and examined its properties. It rapidly converts amylo- and erythro-dextrin into achroodextrin, but it only possesses a very limited saccharifying power. It hydrolyses starch, giving about 40% of maltose, at which point the amylo- and erythro-dextrins are destroyed and the saccharification is completely stopped. Achroodextrinase is also distinguished from other amylases in that the products of saccharification have a much lower viscosity. This new diastase is precipitated by alcohol and by ammonium sulphate. Its optimum temperature is 40°. It acts very well in neutral solutions, and is very resistant to alkalis, but very sensitive to acids. W. G.

Ivy-peroxydase, a Gluco-protein, and G. Woker's Aldehyde-Hypothesis of the Peroxydases. A. W. VAN DER HAAR (*Ber.*, 1917, **50**, 303—305).—In her recent paper (this vol., i, 61) Woker referred to the author's communication on ivy-peroxydase (A., 1910, i, 604) in support of her theory. A protest is raised that

such an interpretation of the conclusions reached by van der Haar was not justified. J. C. W.

Thiophen Series. VII. Thiophen Compounds containing Mercury or Arsenic. WILHELM STEINKOPF (*Annalen*, 1917, **413**, 310—333. Compare A., 1915, i, 155).—It has been shown previously (A., 1914, i, 427) that negatively substituted thiophens behave differently towards mercuric chloride in that 2-halogenothiophens, like thiophen itself, yield normal mercurichlorides, whilst 2-nitrothiophen reacts in another sense. It is now shown that thiophen-2-carboxylic acid in alcoholic solution reacts with cold, saturated mercuric chloride solution and 33% sodium acetate solution to form two amorphous substances, $C_5H_3O_2ClSHg$, decomp. 297—298°, which behave alike in most respects. They are both soluble in dilute aqueous sodium hydroxide or carbonate, but only one dissolves in dilute ammonia; the other, after solution in alkali hydroxide and reprecipitation by dilute hydrochloric acid, acquires the property of dissolving in dilute aqueous ammonia. The two substances are regarded as two forms of *thiophen-2-mercurichloride-5-carboxylic acid*, $CO_2H\cdot C_4H_2S\cdot HgCl$.

The reaction between sodium iodide (1 mol.) and thiophenmercurichloride previously described (*loc. cit.*) leads to the expectation that by the use of 2 mols. of sodium iodide the formation of the thiophenmercuri-iodide will be superseded and mercury dithienyl produced in almost quantitative yield. This is found to be the case; $2C_4H_3S\cdot HgCl + 4NaI = Hg(C_4H_3S)_2 + 2NaCl + HgI_2,2NaI$ and $2C_4H_3S\cdot HgI + 2NaI = Hg(C_4H_3S)_2 + HgI_2,2NaI$. A whole series of thiophen derivatives containing mercury have been examined for their behaviour towards sodium iodide (1 and 2 mols.) in acetone solution. When 1 mol. is used, only 2-iodothiophen-5-mercurichloride behaves like thiophenmercurichloride, and yields a mixture of *2-iodothiophen-5-mercuri-iodide*, $C_4H_2IS\cdot HgI$, faintly yellow, microcrystalline substance, m. p. 141—142° (to a turbid liquid clarifying at about 165°), and *mercury* 5 : 5′-*di-iodo*-2 : 2′-*dithienyl*, $Hg(C_4H_2IS)_2$, pale yellow needles, m. p. 231°; the other substances examined, 2-chloro- and 2-bromo-thiophen-5-mercurichloride, 3 : 4-dimethylthiophen-2-mercurichloride and 2 : 5 - dimethylthiophen-3-mercurichloride, are converted only into the corresponding mercuri-iodides when 1 mol. of sodium iodide is used. It has been found that, when mercurichlorides react with 2 mols. of sodium iodide or mercuri-iodides with 1 mol., all derivatives containing mercury in the α-position yield mercury dithienyls, whereas 2 : 5-dimethylthiophen-3-mercurichloride, the only substance examined containing mercury in the β-position, remains unchanged. If this difference proves to be a general one, the behaviour with sodium iodide in acetone solution is a simple method of distinguishing between the α- and β-derivatives.

All mercury dithienyls behave alike with mercuric haloids in acetone solution, in accordance with the equation $Hg(C_4H_3S)_2 + HgX_2 = 2C_4H_3S\cdot HgX$, where X = Cl, Br, or I. Mercury diphenyl and di-α-naphthyl also react with mercuric chloride in the sense of this equation.

The following new compounds have been prepared by the preceding methods: *2-chlorothiophen-5-mercuri-iodide*, colourless leaflets, m. p. 126—126·5°; *mercury* 5 : 5′-*dichloro*-2 : 2′-*dithienyl*, silvery crystals, m. p. 155°; *2-chlorothiophen-5-mercuribromide*, felted crystals, m. p. 189—190°; *2-bromothiophen-5-mercuri-iodide*, small crystals, m. p. 119°; *mercury* 5 : 5′-*dibromo*-2 : 2′-*dithienyl*, felted crystals, m. p. 183°; *2-bromothiophen-5-mercuribromide*, felted needles, m. p. 197—197·5°; *2-iodothiophen-5-mercuribromide*, almost colourless, felted crystals, decomp. 176° (slowly heated) or about 190° (rapidly heated); 3 : 4-*dimethylthiophen-2-mercuri-iodide*, faintly yellow leaflets, m. p. 142°; *mercury* 3 : 4 : 3′ : 4′-*tetramethyl*-2 : 2′-*dithienyl*, felted mass, m. p. 155—156°; 2 : 5-*dimethylthiophen-3-mercuri-iodide*, colourless needles, m. p. 175°; and *mercury* 2 : 5 : 2′ : 5′-*tetramethyl*-3 : 3′-*dithienyl*, crystals, m. p. 144—145°, prepared by the old method (*loc. cit.*) of boiling 2 : 5-dimethylthiophen-3-mercurichloride with sodium in xylene.

[With MARTIN BAUERMEISTER.]—Direct arseniation of the amino- and hydroxy-derivatives of thiophen is impracticable owing to the difficulty of preparing these substances. Arsenic trichloride, however, reacts with mercury dithienyls or thiophenmercurihaloids in some cases (compare Finzi, A., 1916, i, 94; Finzi and Furlotti, *ibid.*, i, 95). Thus, when arsenic trichloride is shaken in the cold with powdered mercury 2 : 2′-dithienyl and the product is distilled in a vacuum in an atmosphere of hydrogen, fractions are obtained from which the following have been isolated: (1) *thienyldichloroarsine*, $C_4H_3S\cdot AsCl_2$, faintly brown liquid with an unpleasant odour, b. p. 118—122°/11 mm.; (2) *dithienylchloroarsine*, $(C_4H_3S)_2AsCl$, b. p. 219—232°/13 mm.; and (3) *trithienylarsine*, $(C_4H_3S)_3As$, faintly yellowish-green, almost odourless, viscous liquid, b. p. 199—200·5°/0·5 mm. Dithienylchloroarsine, b. p. 106—110°/0·5 mm., is the chief product isolated when thiophen-2-mercurichloride and arsenic trichloride are heated in boiling toluene for many hours, and the product is distilled in the vacuum of a Gaede pump. C. S.

Physiological Chemistry.

Oxyhæmoglobin Crystals from the Blood of Guinea-pigs. OTTO KRUMMACHER (*Zeitsch. Biol.*, 1917, **67**, 272—278).—The crystals of oxyhæmoglobin of the blood of guinea-pigs are not regular tetrahedra, but sphenoids belonging to the rhombic system.

S. B. S.

Cataphoretic Investigations with Thrombin and Fibrinogen. ALFRED RESCH (*Biochem. Zeitsch.*, 1917, **78**, 297—307).—Thrombin, or its negatively charged part, wanders towards the

anode. It dissociates partly into $\left(R{<}^{NH_3X}_{CO_2}\right)^-$ and Ca^+ and partly with the formation of complex organic cations and anions; the anodic complex probably holds calcium in a physically adsorbed form. The charge on the thrombin or its anion is not influenced by the acidity of the solution varying between $p_H=5$ and $p_H=8$. Fibrinogen acts as an electrically neutral substance. The author discusses the bearing of his results on the mechanism of clotting. S. B. S.

The Influence of Extracts of the Genital Glands on Phosphorus Metabolism. JEAN (*Compt. rend.*, 1917, **164**, 438—440).—The injection of an extract of the interstitial gland from the testes of pigs or of an extract of active yellow bodies from the ovaries of sows causes a marked diminution in the phosphorus excretion of humans, whether on a diet slightly lacking in phosphorus or containing it in slight excess. W. G.

The Sulphur Compounds of the Urine. E. SALKOWSKI (*Biochem. Zeitsch.*, 1917, **79**, 68—80).—Thiosulphate is found in the urine of rabbits after feeding on cabbage. The precursor of this is to be found in the aqueous extract of the vegetables, but not in the residue after extraction of the vegetables with water. No thiosulphate is found in human urine after ingestion of cabbage. Ethyl mercaptan is also found in rabbits' urine after ingestion of cabbage, in the form of an unknown compound, from which it can be obtained after scission with hydrochloric (but not acetic) acid. Ethyl sulphide is found in the urine of dogs in the form of a compound, from which it can be obtained by the action of calcium hydroxide. The parent substance is apparently a sulphonium base. The author reviews the literature dealing with the presence of cystine in urine. Experiments are quoted which seem to indicate that the thiocyanates of urine are derived from glycine. The factors influencing the relationship of "neutral" to the total sulphur of the urine are also discussed. S. B. S.

Relation between Chemical Constitution and Physiological Action in Certain Substituted Aminoalkyl Esters. II. FRANK LEE PYMAN (T., 1917, **111**, 167—172. Compare T., 1908, **93**, 1793).—It is already known that the substitution of benzoyl by phenylacetyl in cocaine yields a product devoid of local anæsthetic properties, whereas with *α-eucaine* a similar change produces a compound possessing such properties, and the author has now examined the effect of a similar replacement in anæsthesine (ethyl *p*-aminobenzoate) and novocaine (*β*-diethylaminoethyl *p*-aminobenzoate). Ethyl *p*-aminophenylacetate (Salkowski, A., 1895, i, 602) dissolved in olive oil and *β-diethylaminoethyl* p-*aminophenylacetate*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$ (obtained by reduction of the corresponding p-*nitrophenylacetate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2),$$

in the form of an aqueous solution of the hydriodide, were devoid of local anæsthetic power.

In extension of the earlier observation (*loc. cit.*) that the salts of aminoalkyl esters of the general formula,

$$CH_2R\cdot CH(OBz)\cdot CH_2\cdot OBz$$

(where $R = NMe_2$, NEt_2, or $C_5H_{10}N$), possessed considerable local anæsthetic action, but were also toxic and irritant, compounds of a modified type were prepared. By the interaction of phenyl glycide ether and diethylamine there was obtained *β-diethylamino-β′-phenoxy*iso*propyl alcohol*, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NEt_2$, of which the *benzoyl* derivative gave solutions which were too strongly acidic for satisfactory physiological examination; the hydrochloride of the amino-alcohol, however, in aqueous solution, produced a distinct degree of local anæsthesia. 8-*Benzoyloxy*-1-*methyl*-1:2:3:4-*tetrahydroquinoline*, prepared by benzoylating its parent compound, gave a hydrochloride so strongly acidic that it could not be tested physiologically, and an endeavour to prepare the corresponding *p*-aminobenzoyl derivative by way of 8-p-*nitrobenzoyloxy*-1-*methyl*-1:2:3:4-*tetrahydroquinoline* miscarried on account of the ease with which the nitrobenzoyl radicle undergoes hydrolytic scission. p-*Aminobenzoyl*-p-*phenetidine*, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, prepared by reduction of the corresponding *nitro*-compound, was found to be almost insoluble in water and caused no local anæsthesia when introduced as a powder into the conjunctival sac. D. F. T.

Anæsthesine and Isethionyl-*p*-aminobenzoic Acid. E. Salkowski (*Biochem. Zeitsch.*, 1917, **79**, 81—95).—An account of experiments, which did not lead to the desired result, for obtaining a soluble compound of anæsthesine (ethyl *p*-aminobenzoate) is given. Special attention was given to the condensation product of anæsthesine with isethionic acid (compare A., 1916, i, 815). This isethionyl-*p*-aminobenzoic acid, when administered to rabbits, undergoes scission, and sulphuric acid and (in smaller quantity) thiosulphuric acid are excreted in the urine. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **79**, 35—50).—The following substances were found to stimulate the formation of a urease by bacteria: dextrose, *d*-galactose, glycerol, *dl*-glyceraldehyde, dihydroxyacetone, pyruvic acid, and lactic acid. The stimulatory action of these substances was great. A stimulatory action was shown, but less markedly, by *d*-lævulose, *d*- and *l*-arabinose. Mannose, *d*-sorbose, rhamnose, heptose, the polysaccharides, glucosides, and the sugar alcohols were without action. S. B. S.

The Production of Phenol by Bacteria. ALBERT BERTHELOT (*Compt. rend.*, 1917, **164**, 196—199).—The author has isolated from

the intestinal flora of human subjects suffering from chronic intestinal trouble a bacillus, which he calls *Bacillus phenologenes*, which is capable of producing, under average culture conditions, about ten times as much phenol as the most active known phenologenic species. With *l*-tyrosine as the only organic nutrient, under the most satisfactory conditions it can produce, in fifteen days at 37°, 800 mg. of phenol per litre, the yield thus reaching about 80% of the theoretical yield. The bacillus is anærobic. W. G.

Biochemical Properties of Paratyphus Bacilli. H. C. DE GRAFF (*Bull. Sci. Pharmacol.*, 1916, **23**, 257—266; from *Chem. Zentr.*, 1917, i, 332).—The decomposition of proteins, peptides, and amino-acids by paratyphus bacilli has been studied, the materials used being centrifuged milk, peptone (Roche and Witte), tryptophan, tyrosine, and alanine. The paratyphus bacillus B degrades proteins and peptides to amino-acids, and can eliminate the amino-group from the latter and oxidise them to acids poorer by one C-atom than the amino-acids themselves. The paratyphus bacillus A acts similarly towards amino-acids, but does not decompose proteins or peptides. The formation of indole from tryptophan or phenol from tyrosine was not observed, but these amino-acids yield indoleacetic acid and *p*-hydroxyphenylacetic acid in addition to small amounts of indolecarboxylic acid and *p*-hydroxybenzoic acid. Alanine gives acetic acid, but not formic acid; Witte's peptone yields tryptophan and indoleacetic acid, and Roche's peptone gives *l*-tyrosine. Both types of bacillus cause the formation of small amounts of acid from the lactose of milk, but only the B variety decomposes the proteins energetically with the liberation of ammonia. Milk treated with litmus is more or less strongly reddened at first by both types of bacillus, but is only quickly coloured blue by the paratyphus bacillus B. H. W.

The Relationship between the Capacity for Killing and Inhibiting the Growth of Germs and the Valency. E. FRIEDBERGER and G. JOACHIMAGLU (*Biochem. Zeitsch.*, 1917, **79**, 135—151).—In experiments with bacteria and protozoa it can be shown that the tervalent arsenic compounds (sodium arsenite and salvarsan) have a greater toxic effect than the quinquevalent compounds (sodium arsenate and atoxyl). A similar difference is noted between the tervalent (tartar emetic) and quinquevalent (potassium pyroantimoniate) antimony compounds. Arsenites inhibit the action of yeast to a greater extent than do arsenates. S. B. S.

Ferment Action. I. The Fermentative Degradation of Polypeptides. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforschung*, 1916, **1**, 533—596; from *Chem. Zentr.*, 1917, i, 311—313).—The authors have investigated the action of ferments on synthetic polypeptides which are formed from such amino-acids as occur naturally. Even in these circumstances many unknown factors are found to enter into the problem. The physical properties of the substrate in the solution, as well as its chemical constitu-

tion, are of importance, as well as the unexplained condition of the ferment. With respect to the latter, the authors have secured uniformity by performing all comparative experiments with one and the same solution of the ferment prepared in a definite manner. Uniform conditions were also maintained in other respects, and it is emphasised that the results obtained are only valid under these conditions and do not apply, for example, to processes within the cell. Solutions of the ferment were prepared from dried yeast according to Lebedev; it was found that different consignments of the preparation from the same firm showed considerable differences in activity. Strictly comparable experiments were therefore always carried out with the expressed juice of yeast from a single consignment. The juice was fairly acid to litmus, and was therefore nearly neutralised, since otherwise the desired regulation of the solutions could not be obtained. The turbidity caused by neutralisation (obviously protein) disappeared after some hours, particularly rapidly at 25°. Freshly prepared extracts increased in activity when preserved, the maximum being attained more rapidly at 25° than at 0°. Thereby, the optimum of the reaction in experiments with glycyl-*l*-leucine is displaced in the direction of greater hydroxyl-ion concentration. Addition of very minute amounts of protein to the freshly prepared extracts causes an immediate exaltation of activity which does not then further increase, whilst larger quantities bring about a diminution. Apparently, therefore, surface phenomena are intimately concerned with the increase in activity. To avoid these complications, the yeast-juice was preserved until constant in its behaviour towards glycyl-*l*-leucine as substrate. The reverse change, namely, decrease in activity due to destruction of the ferment, occurs in older extracts. The greatest stability of peptase occurs with a hydrogen-ion concentration of about 3×10^{-7}; variation in either direction causes a distinct decomposition after one hour at 25° and the sensitiveness is greater towards an increase in the hydrogen-ion than towards an increase in the hydroxyl-ion concentration. In the experiments described by the authors, in which the duration did not exceed forty minutes and the hydrogen-ion concentration lay generally within the limits $p_H = 6{\cdot}5$—$8{\cdot}5$, the correction involved for this reason was too small to be taken into account.

The rate of fission of glycyl-*l*-leucine was studied by adding 10 c.c. of a solution containing 0·4 gram of the dipeptide to 20 c.c. of a phosphate solution of the desired hydrogen-ion concentration; the mixture was warmed to 25° and treated with yeast extract (2 c.c.) previously warmed to 25°. The amino-nitrogen was estimated after definite intervals by Sörensen's method in the presence of formaldehyde. Parallel with these experiments, the electromotive force against a $1/10N$-calomel electrode was measured. Control experiments with mixtures of yeast and regulator, or regulator and polypeptide solution are unnecessary, since they remain unchanged under the experimental conditions. The course of the degradation of the dipeptide at different $H^{\cdot}$ and OH' concentrations was thus followed, and it was found that not merely the rate of reaction but

also its nature is dependent on them. Similar experiments were performed with *d*-alanyl-*d*-leucine; the influence of variation in the amount of ferment on the fission of glycyl-*l*-leucine between p_H 7·5 and p_H 7·13 was also investigated. Similar experiments, but in more dilute solution, were also performed with six dipeptides which form three pairs of isomerides (namely, glycyl-*l*-leucine, *l*-leucylglycine, glycyl-*d*-alanine, *d*-alanylglycine, *d*-alanyl-*l*-leucine, *l*-leucyl-*d*-alanine), in which hydrolysis occurred much more rapidly. The experimental results are expressed in tables and curves.

Increase in the concentration of the yeast extract greatly diminishes the rate of reaction, but this depends also on the reaction and on the amount of yeast peptase present. It is true for glycyl-*l*-leucine in very dilute acid or faintly alkaline solution (p_H = 6·20—7·50) in the presence of an excess of yeast extract, whilst increase of an originally very small amount in this interval increases the amount hydrolysed. Beyond $p_H = 8$, a quantity of yeast extract which previously diminished the reaction velocity, is found to cause a further increase. In all cases in which the graphs have a parabolic form, the quantity of material hydrolysed is approximately proportional to the square root of the time, and approximately equal amounts of polypeptide are hydrolysed for equal values of $F \times t$ (F = concentration of ferment, t = time). Special experiments have shown that the amino-acids which are formed as products of hydrolysis can exert a powerful retarding action; glycine behaves thus in alkaline, *l*-alanine, and *d*-leucine only in acid solution. This is contrary to the assumption of Herzfeld (A., 1915, i, 468) that the degradation products behave as accelerators.

A specific action of the substrate is certainly concerned with the influence of the concentration of the ferment, but it has not yet been proved whether such action depends on physical characteristics or chemical affinities. Only glycyl-*d*-alanine behaves similarly to glycyl-*l*-leucine, whilst, for example, with *l*-leucylglycine quantities of juice which caused the effects described above bring about a uniform increase in the rate of reaction independent of the acidity of the solution. The course of the reaction is probably mainly governed by diffusion processes. The authors discuss the possibility of explaining the linear course of the reaction in faintly acid solution by assuming the formation of a compound of ferment and substrate or by autocatalytic action, but do not put forward a hypothesis which satisfactorily covers all cases.

The optimal hydrogen-ion concentration has been determined for a number of polypeptides with the following results, the values of p_H being enclosed within brackets: glycyl-*l*-leucine (8·41, 8·50); *l*-leucylglycine (7·50, 7·56); *d*-alanylglycine (7·30—8·13); glycyl-*d*-alanine (7·30—7·91); *d*-alanyl-*l*-leucine (6·76, 6·85); *l*-leucyl-*d*-alanine (6·80—7·89); *dl*-leucyl-*l*-aspartic acid, 2% (6·76); *dl*-leucyl-*l*-aspartic acid, 10% (6·80); *l*-leucylglycylglycine (7·26); *l*-leucyldiglycylglycine (7·29); *l*-leucyltriglycylglycine (7·28); *l*-leucylpentaglycylglycine (6·24).

The optima for the different polypeptides with equal amounts of

ferment depends on their nature, those which are formed from like components showing a generally, but not perfectly uniformly, comparable behaviour. The occurrence of an optimum is regarded as the result of two opposed forces, the diffusion of the substrate into the ferment phase and the adsorption of the fission products by the latter. Both are favoured by hydroxyl ions.

The results which have been obtained support the view that ferments act as colloidal catalysts and are closely connected with the work of Bredig and his co-workers on 'inorganic ferments.' Further experiments are required to determine what causes bring about diffusion to the surface of the disperse ferment phase and whether these are connected with the specific nature of ferment action. The assumption that a ferment is active towards a definite grouping of atoms is not supported by the authors' experiments.

H. W.

The Oxidative Actions of Yeast. G. Färber (*Biochem. Zeitsch.*, 1917, **78**, 294—296).—The author finds that, contrary to the experience of Herzog, saligenin is not oxidised to salicylic acid by yeast, nor could he trace any chemical changes of thymol and cymol. S. B. S.

The Detection of Tyrosol and Tryptophol in Products of Fermentation. Felix Ehrlich (*Biochem. Zeitsch.*, 1917, **79**, 232—240).—In the case of wine, the liquid is evaporated to a syrup in a vacuum, the residue dissolved in alcohol, the solvent distilled off, and the residue thus obtained heated with a 10% solution of sodium hydroxide, to saponify the esters of the alcohols. The tryptophol is extracted from this alkaline liquid by ether. If no crystals of tyrosol can be obtained, its presence can be determined by the author's dimethylaminobenzaldehyde reagent, which gives a characteristic bluish-red colour on warming and addition of hydrochloric acid, the product being soluble in amyl alcohol, in which solution it can be examined spectroscopically. The tyrosol can be obtained from the alkaline solution (after the saponification with sodium hydroxide as mentioned above) by making this first slightly acid with sulphuric acid, then slightly alkaline with sodium hydrogen carbonate, and then extracting for twenty hours with ether. After distilling off the ether, a residue is obtained which yields crystals of tyrosol; this can also be obtained in the form of its dibenzoyl derivative. Similar methods for obtaining tyrosol and tryptophol can be applied to beer and mash. S. B. S.

The Vegetation of Yeasts and Moulds on Heterocyclic Nitrogen Compounds and Alkaloids. Felix Ehrlich (*Biochem. Zeitsch.*, 1917, **79**, 152—161).—Experiments were carried out with the following organisms: *Willia anomala, Oidium lactis, Pichia farinosa, Penicillium glaucum, Aspergillus niger*, and the following nitrogenous substances: pyridine, piperidine tartrate, coniine, nicotine, cinchonic acid, quinine, brucine, cocaïne, and morphine. It was shown that these could serve as a source of nitrogen to the organisms. S. B. S.

Production of Pyruvic Acid by Biochemical Oxidation of Lactic Acid. P. MAZÉ and M. RUOT (*Compt. Rend. Soc. Biol.*, 1916, **79**, 706—710. Compare Mazé, A., 1913, i, 567; Fernbach and Schoen, A., 1914, i, 237, 910).—*Amylomyces Rouxii* (a mould related to *Mucor*) and another undetermined fungus, parasitic on maize, oxidise lactic acid to pyruvic acid in a solution containing no other carbon compound, and ultimately also destroy the pyruvic acid formed. The yield is better with free lactic acid than with calcium lactate, for in the latter case the solution becomes alkaline and growth is inhibited. As may be foreseen, the respiratory quotient is low (0·77—0·90). Similar effects may be obtained with sucrose in thin layers of a solution not more concentrated than 1 per cent. (in order to avoid the formation of alcohol). G. B.

Evidence of the Existence in Malt of an Enzyme Hydrolysing the Furfuroids of Barley. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (T., 1917, **111**, 121—130).—Having observed the presence of a slightly increased percentage of furfuroids (furfuraldehyde-yielding matter) in rootlet-free malt as compared with the original barley, and that in the rootlets and husks of the malt the furfuroid content is higher than in the barley as a whole, the authors allowed embryos excised from barley to germinate in the dark on sterilised sand soaked with sucrose solution, and found an increase in weight and in furfuroid content, the embryo presumably having effected the conversion of sucrose into a poly-pentose.

When allowed to germinate between damp linen in a normal manner, barley corns were found to undergo no increase in total furfuroid content, the increased furfuroid content of the embryo being approximately equal to the corresponding diminution observed in the endosperm. This result appears to indicate the existence of an enzyme capable of hydrolysing insoluble furfuroids in the non-embryo portion of the grain, so that the soluble products may be transferred to the embryo. Confirmation of this view is supplied by the facts that malt contains a higher proportion of soluble furfuroids than the corresponding barley, and that a mixture of green malt and barley when digested with water at 35° gives a higher yield of soluble furfuroid matter than the average for barley and malt separately; also it was found that the enzymes, which are precipitated on the addition of an aqueous infusion of malt to alcohol, when dissolved in water are capable of hydrolysing 10% of the insoluble furfuroids of purified malt husks to soluble furfuraldehyde-yielding substances. The evidence therefore indicates the existence in green malt of a "pentosase" capable of hydrolysing insoluble furfuroids. D. F. T.

The Organic Matter of the Soil. I. Some Data on Humus, Humus Carbon, and Humus Nitrogen. ROSS AIKEN GORTNER (*Soil Sci.*, 1916, **2**, 395—441).—"Humus" extracts were made from seventeen samples representing soils, peats, and fresh

vegetable matter, 4% ammonia solution being used with and without a preliminary leaching with 1% hydrochloric acid. The humus obtained was very similar in all cases, indicating that it is not a typical soil product, but may also be obtained from unchanged vegetable matter. When the ammonia was replaced by a 4% solution of sodium hydroxide in the preparation of the extracts, neither the same substances nor the same quantity of the substances were obtained, the extracts with sodium hydroxide containing more carbon and being less deeply coloured.

The nitrogen compounds in the soil were shown to be somewhat more insoluble than those in fresh vegetable matter by the fact that 1% hydrochloric acid dissolved 20% of the total nitrogen from the fresh vegetable matter and only 3—4% from the soils and peats; also that whilst about 30% of the nitrogen in the soils was insoluble in the sodium hydroxide, the nitrogen in the fresh vegetable matter was dissolved almost completely.

When the samples were treated successively with 4% sodium hydroxide, with 1% hydrochloric acid, again with sodium hydroxide, and finally shaken up with water, the fresh vegetable matter and an acid peat yielded colourless solutions, but in the case of all the other soils jet-black solutions were obtained, from which "soil pigment" was precipitated by acids or alkalis. Having estimated the amount of carbon in this black pigment, it was calculated that probably not more than 30—40% of the humus (so-called "matière noire" of Grandeau) dissolved by ammonia could be made up of really black compounds, the rest consisting of colourless substances. The author points out that the black pigment appears to be the only substance which can be said to be a true soil product. It contains only a relatively small proportion of the soil nitrogen, and would seem to have but little importance in the problem of soil fertility. L. M. U.

The Organic Matter of the Soil. III. The Production of Humus from Manures. ROSS AIKEN GORTNER (*Soil Sci.*, 1917, **3**, 1—8).—Organic matter, in the shape of powdered silk waste, powdered wool, flour, or lucerne meal was added to soil at the rate of 3—7% of the soil. Each mixture was put into a pot in a greenhouse and left for a year, so that humification should take place. Estimations of carbon, nitrogen, and "humus" soluble in 4% ammonia were made on the original mixtures and on the final product. They were considerably lower after storage than before, the losses amounting to from 8 to 55% of the original carbon, from 5 to 26% of the original nitrogen, and from 6 to 33% of the original "humus." The author is of opinion that the maximum amount of "humus" is therefore present in a soil immediately after a green manure crop has been ploughed in and before the "humifying" bacteria or fungi have begun their work.

L. M. U.

Soil Solution obtained by the Action of a Hydraulic Press. G. RAMANN, S. MÄRZ, and H. BAUER (*Int. Mit. Bodenkunde*, 1916, **6**, 27; from *Bied. Zentr.*, 1917, **46**, 6).—The authors point

out that the analysis of drainage waters from soils does not afford an accurate means of determining the composition of the normal soil solution, as drainage only occurs when the soils are super-saturated. For this reason they adopted the method of forcing water out of the soil with a hydraulic press. Samples of 3 kilos. of soil were taken from the fields and subjected to a pressure of 300 kilos. to the square cm., the liquid expressed being then analysed for calcium, magnesium, sulphates, phosphoric acid, and potassium. The sampling was done on six different occasions over a period lasting from May to October; both surface and subsoil were used.

The calcium content was found to vary considerably in the surface soil, but in the subsoil it seemed fairly constant, except for a rise in mid-summer. Potassium, contrary to the generally accepted view, behaved very much like calcium, that is, its content fluctuated according to the general concentration of the soil solution, rising when evaporation took place and being lowered by spells of wet weather. Further, there was evidence of potassium and calcium being transported from the subsoil to the surface during a prolonged period of drought, but no evidence was obtained that adsorption exerted any regulating effect on the concentration of the soil solution. The exchange of bases only occurred when the proportion which the dissolved substances bore to one another was altered.

The authors suggest that the selective action of the plant roots, by throwing the soil solution out of equilibrium, would have a considerable effect in bringing fresh supplies of nutrient substances into solution. They state also that the pressure method of obtaining soil water is only applicable in the case of soils made up of very fine particles or containing a considerable amount of humus.

L. M. U.

Criticism of the Use of Superphosphates in Agriculture. NICOLA ALBERTO BARBIERI (*Gazzetta*, 1917, **47**, i, 38—51).—From the results of a number of experiments the author draws the following conclusions: The whole of the phosphorus contained in plants occurs in the form of phosphoric acid united with alkalis, alkaline earths, and possibly other mineral bases. When the soluble and the insoluble phosphates are eliminated, the plant contains no trace of any other compound of phosphorus; phytins are, consequently, lacking. Plants do not contain and do not absorb mono- or di-calcium phosphates (superphosphates). Superphosphate exerts a retarding action on the germination of seeds and on the development of plants, and cereals and leguminous plants grown in soil fertilised by means of superphosphate contain less total phosphorus than those from contiguous soil not treated with the superphosphate. Further, superphosphate destroys seeds with which it comes into direct contact. Where mineral fertilisation is to be effected it is best to apply those mineral substances which the plants themselves contain.

T. H. P.

Organic Chemistry.

Action of Bromine Water on Ethylene. JOHN READ and MARGARET MARY WILLIAMS (T., 1917, **111**, 240—244).—It has already been observed (Pope and Read, T., 1912, **101**, 760) that bromine water in its action on indene behaves like a solution of hypobromous acid, yielding bromohydroxyhydrindene, and it is now shown that bromine water exhibits a similar reaction with ethylene, giving ethylene bromohydrin accompanied by an approximately equal weight of ethylene dibromide. This behaviour is evidently due to the existence of the equilibrium $Br_2 + H_2O \rightleftarrows HBr + HOBr$.

For experimental details see the original. D. F. T.

Pyrogenic Acetylene Condensations. IV. RICHARD MEYER and HANS WESCHE (*Ber.*, 1917, **50**, 422—441. Compare A., 1912, i, 525; 1913, i, 1294; 1915, i, 207).—Mixtures of acetylene with hydrogen sulphide, ammonia, or steam have been heated in the electric oven already described in order to find whether the resultant tars contained any of the phenolic or heterocyclic compounds found in coal tar. The treatment of the tar is fully described, and the original should be consulted for the details.

Acetylene and hydrogen sulphide are found to react at 640—660° to form thiophen, and most probably thionaphthen and thiophthen. Acetylene, purified coal gas (equivalent to methane), and hydrogen sulphide give α- or β-thiotolen (identified as *tetrabromothiotolen*, $C_4Br_3S{\cdot}CH_2Br$, pale yellow, pearly leaflets, m. p. 113—114°), thioxens (colour reactions), thionaphthen, and thiophthen (from which *tetrabromothionaphthen*, very long, slender needles, m. p. 229—230°, was prepared and analysed).

Acetylene and ammonia give pyridine, pyrrole, aniline, benzonitrile, naphthalene, quinoline, indole (?), fluorene, and anthracene.

With steam, the condensation proceeds at a lower temperature (500—600°), and a small quantity of phenol is obtained. Acetylene, steam, and ammonia together give pyridine, aniline, phenol, and much hydrogen cyanide.

A mixture of aniline and steam reacts at 650—700° to give a small quantity of phenol and also some carbazole. When a dilute solution of phenol in water is distilled through an iron tube heated at 930°, more than 90% of the substance suffers decomposition, naphthalene and gases being produced. J. C. W.

The Volatile Reducing Substance in Cider Vinegar. R. W. BALCOM (*J. Amer. Chem. Soc.*, 1917, **39**, 309—315. Compare Farnsteiner, A., 1899, ii, 705; Pastureau, A., 1905, i, 559). —As a result of further experimental work, the author shows that the volatile reducing substances in cider vinegar consist largely,

if not wholly, of acetylmethylcarbinol, which is shown to be a normal constituent of this vinegar. W. G.

The Ethyl Hydrogen Sulphate Reaction. P. N. EVANS and J. M. ALBERTSON (*J. Amer. Chem. Soc.*, 1917, **39**, 456—461. Compare Claësson, A., 1879, 775).—A study of the reaction $EtOH + H_2SO_4 \longrightarrow EtHSO_4 + H_2O$, with the view of determining its speed and degree of completeness, over a temperature range of 20—140°.

The results show that the reaction between equimolecular quantities of ethyl alcohol and sulphuric acid is about 58—60% complete when equilibrium is reached between 20° and 100°. The time required for equilibrium to be established varies from 150 minutes at 20° to 10 minutes at 70° and higher temperatures. The reaction is very slowly reversible if water is added, no difference in the acidity being noticeable after twenty-four hours at the ordinary temperature. From 70° upwards ether is formed with increasing rapidity, the acidity thus tending to rise again from its minimum with lapse of time. At the ordinary temperature there is a very slow formation of one or all of the three compounds, ethyl sulphate, isethionic acid, and ethionic acid, this being evidenced by a loss of 4% of the acidity in three weeks. W. G.

Heavy Oil of Wine. ROBERT KREMANN (*Monatsh.*, 1917, **38**, 53—62).—When 2·5 parts of concentrated sulphuric acid and 1 part of ethyl alcohol are distilled on a sand-bath, a product is obtained which settles into two layers. The lower layer is a yellow, oily liquid, formerly termed heavy oil of wine. This consists mainly of ethyl sulphate, but contains a small quantity (5%) of unsaturated hydrocarbons of the olefine series. An investigation of this oil is the subject of the present paper. On shaking with warm water, the whole of the ethyl sulphate is hydrolysed to ethyl hydrogen sulphate, which passes into solution, whereas the hydrocarbons remain undissolved. The hydrocarbon oil was collected and dried; it boiled at 280° and had D = 0·921. On keeping, a solid, crystalline substance separated of D = 0·980, m. p. 100°, b. p. 260°. This also is an olefine. Molecular weight determinations by the cryoscopic method (in acetic acid) and by the ebullioscopic method (in ether) showed that the liquid hydrocarbon has a mean molecular weight of 224, that is, $C_{16}H_{32}$, although in all probability a mixture of hydrocarbons is really present. The amount of the solid hydrocarbon was too small to allow of similar experiments being made. The author then carried out a series of hydrolysis experiments of the crude ethyl sulphate in aqueous, acid, and alkaline solutions, similar to those previously carried out with pure ethyl sulphate (A., 1907, ii, 157). The results obtained in these experiments led him to the conclusion that the crude ethyl sulphate prepared as above is not a mixture of ethyl sulphate and unsaturated hydrocarbons, but rather a mixture of ethyl sulphate and a compound of ethyl sulphate with the unsaturated hydrocarbons. J. F. S.

The Nitrogenous Hydrolysis Products of Heart Lecithin. C. G. MacArthur, F. G. Norbury, and W. G. Karr (*J. Amer. Chem. Soc.*, 1917, **39**, 768—777).—Lecithin has been prepared from ox-heart and hydrolysed by boiling with $4\frac{1}{2}\%$ hydrochloric acid. About 12% of its nitrogen is in a form insoluble in water after hydrolysis. Of the soluble nitrogen, about one half is in the form of choline and the other half in the form of aminoethyl alcohol. The very small amount of ammonia in the hydrolysed solution is probably a contamination. The amount of amino-acid nitrogen was also very small. Heart lecithin has practically the same composition as brain lecithin as far as its main constituents are concerned (compare Darrah and MacArthur, A., 1916, i, 366), so that it is possible that the two lecithins are the same compound. Dehydration by means of acetone was found to be the most satisfactory method of preparing the tissue for work on the phosphatides. W. G.

The Inositol Phosphoric Acids of Cottonseed Meal. J. B. Rather (*J. Amer. Chem. Soc.*, 1917, **39**, 777—790. Compare A., 1913, i, 818).—From one sample of cottonseed meal an inositol-phosphoric acid has been isolated in the form of its strychnine salt, corresponding in composition and in the m. p. of its strychnine salt with inositol-triphosphoric acid (compare Clarke, T., 1914, **105**, 535). It does not appear, however, to be a constant constituent of cottonseed meal, since other samples of this meal similarly treated yielded an inositol-phosphoric acid corresponding in composition with inositol-pentaphosphoric acid or to the acid $C_{12}H_{41}O_{42}P_9$ previously reported (*loc. cit.*). The acid gives a *strychnine* salt, m. p. 220—222°. This same acid and its strychnine salt were also obtained by using the method described by Anderson (compare A., 1914, i, 641), by which he reported the isolation of inositol-hexaphosphoric acid. The silver salts of these acids were prepared and analysed. The author deems it best to ascribe the formula $C_6H_6(OH)(H_2PO_4)_5$ of the pentaphosphoric acid to this acid. W. G.

Catalytic Hydrogenation with Formic Acid, and Products of the Catalytic Condensation of Ordinary Acetone. Alph. Mailhe and F. de Godon (*Bull. Soc. chim.*, 1917, [iv], **21**, 61—64). —Formic acid in the presence of certain finely divided metals and metallic oxides is decomposed, giving carbon dioxide and hydrogen (compare Sabatier and Mailhe, A., 1912, i, 156). This reaction, copper and nickel being the catalysts, has been used for the hydrogenation of certain aromatic ketones at 300°. In this way, acetophenone, phenyl ethyl ketone, phenyl butyl ketone, phenyl propyl ketone, phenyl *iso*propyl ketone, benzyl *iso*propyl ketone, benzophenone, phenyl benzyl ketone, and *p*-tolyl benzyl ketone have readily been reduced to the corresponding hydrocarbons.

When this reaction was applied to acetone, the mixed vapours of acetone and formic acid being passed over finely divided nickel at 300°, the products were mesityl oxide, β-methylpentan-δ-one, a

little valerone, and a more condensed product, b. p. 250°. The mesityl oxide is first formed from the acetone, and then undergoes partial or total hydrogenation. This preliminary condensation is also brought about by thoria at 410—420°. W. G.

Chloroethers. I. The Action of Chlorodimethyl Ether on Salts of Organic Acids. FRIEND E. CLARK, S. F. COX, and E. MACK (*J. Amer. Chem. Soc.*, 1917, **39**, 712—716. Compare Litterschied and Thimme, A., 1904, i, 963).—Methyl chloromethyl ether reacts with salts of the aliphatic acids to give methoxymethyl esters. Lead formate gives *methoxymethyl formate*,

$$H\cdot CO_2\cdot CH_2\cdot OMe,$$

b. p. 102—103°, D^0 1·1030, D^{18} 1·0866, D^{25} 1·0777, a clear liquid, with a slightly ethereal odour, burning with a blue flame, and reacting with water to give formic acid, formaldehyde, and methyl alcohol. Fused sodium or potassium acetate gives *methoxymethyl acetate*, b. p. 117—118°, D^0 1·0562, D^{18} 1·0358, D^{25} 1·0280, burning with a purple flame. Fused lead propionate gives *methoxymethyl propionate*, b. p. 133°, D^0 1·0137, D^{18} 0·9945, D^{25} 0·9872. It does not burn very readily, nor is it so easily decomposed with water as the two previous esters. Fused sodium butyrate yields *methoxymethyl butyrate*, b. p. 151—152°, D^0 0·9929, D^{18} 0·9747, D^{25} 0·9678. It is very difficultly inflammable and decomposes with water. The stability of the esters increases with the molecular weight. The introduction of a $\cdot CH_2\cdot$ group produces a rise of about 16° in the boiling point and a decrease in the density. W. G.

Bismuth Acetate. E. SALKOWSKI (*Biochem.-Zeitsch.*, 1917, **79**, 96—104).—The acetate was formed by dissolving the finely divided metal in a mixture of acetic acid and hydrogen peroxide, or by dissolving the hydroxide in acetic acid. A crystalline product, $Bi(C_2H_3O_2)_3$, was obtained, which is unstable and loses acetic acid on keeping in air, and more rapidly in a vacuum. If heated at 125°, it loses acetic anhydride rapidly and yields bismuthyl acetate:

$$Bi(C_2H_3O_2)_3 = BiOC_2H_3O_2 + C_4H_6O_3.$$

The bismuthyl salt, unlike the salt $Bi(C_2H_3O_2)_3$, is insoluble in water. S. B. S.

Studies in Steam Distillation. Propionic, Butyric, Valeric, and Hexoic Acids. H. DROOP RICHMOND (*Analyst*, 1917, **42**, 125. Compare A., 1908, i, 495, 754).—The acids were distilled under the conditions given previously (*loc. cit.*), and the results are given for the values x, y, and a ($x = 1 -$ water distilled %/100; $y =$ acid distilled %/100; $a = \log . y/\log . x$). The value of a for the various acids was: propionic acid, 1·224; butyric acid, 2·00; valeric and *iso*valeric acids, 3·50. In the case of hexoic acid $a = 3·71$, which was much lower than was expected. W. P. S.

The Preparation of Glycollic Acid. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 109—112).—In order to avoid the fractional crystallisation of calcium glycollate necessary in

Hölzer's method for preparing glycollic acid (compare A., 1884, 583) the author has modified the method. The chloroacetic acid (1 part) was heated on a water-bath with water (7 parts) and barium carbonate (2 parts) until no more carbon dioxide was evolved. More water (13 parts) was added and after a time a slight excess of barium carbonate, and the heating continued. The barium was then almost completely precipitated from the hot liquid by adding 95% of the calculated quantity of sulphuric acid, the barium sulphate filtered off, and the filtrate evaporated to a pale yellow syrup. The syrup was left to cool and inoculated with a crystal of glycollic acid and the whole set to a hard cake during the night. This was broken up and exposed to the air to allow the hydrochloric acid to evaporate, the crystals being finally recrystallised from water. Care must be taken during the evaporation to a syrup not to carry the process too far or a gelatinous anhydride separates out. W. G.

The Course of the Reaction which takes place when Higher Unsaturated Fatty Acids are Fused with Potassium Hydroxide. ALFRED ECKERT (*Monatsh.*, 1917, **38**, 1—10).—With the object of examining the mechanism of the reaction between fused potassium hydroxide and the higher unsaturated fatty acids and also of testing the theory put forward to explain this reaction by Wagner (*Ber.*, 1888, **21**, 3353), the author has examined the action of molten potassium hydroxide on several dihydroxy- and monohydroxy-fatty acids with the following results. Dihydroxystearic acid when fused with 6 times its weight of potassium hydroxide, 3 times its weight of water, and 3/5ths its weight of potassium chlorate at 200—220° for ten to twelve hours, yields pelargonic acid and azelaic acid. In the same way, dihydroxybehenic acid yields pelargonic acid and brassylic acid; satavic acid,

$$CH_3\cdot[CH_2]_4\cdot[CH(OH)]_2\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

yields azelaic acid, acetic acid, and hexoic acid; β-keto-stearic acid is practically unacted on. From these results the author draws the conclusion that dihydroxy-acids and monohydroxy-acids are not intermediate products in the decomposition of higher unsaturated fatty acids. Consequently, the probable course of the reaction is to be regarded as the direct shifting of the double linking to the end of the chain. J. F. S.

Fusion Diagram of the System, Methyl Oxalate–Water. ANTON SKRABAL (*Monatsh.*, 1917, **38**, 25—29).—The freezing-point curve for methyl oxalate–water has been constructed. It is shown that methyl oxalate and water in the liquid state are soluble in one another to a limited extent. The ester has m. p. 53·5°, and on the addition of water this is lowered to 48°, at which temperature the ester crystallises out. The eutectic containing 4% of ester melts at $-0·5°$. At 48°, further addition of water has no effect on the freezing point until the mixture contains 84% of water, but over the whole of this range the molten substance consists of two phases. The effect of raising the temperature reduces this region only very

slightly. The values given are only to be regarded as limiting values, since the quantity of ester present is somewhat uncertain owing to the rapidity with which it is hydrolysed by water.

J. F. S.

Condensation Product of Cholic Acid with Formaldehyde. SYNTHETIC PATENTS Co. (U.S. Pat., 1213261; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—A compound of therapeutic value is produced by the combination of cholic acid and formaldehyde. It is a white powder, m. p. about 140°, soluble in alkali, alcohol, and glacial acetic acid.

H. W.

A Relation between the Chemical Constitution and the Optical Rotatory Power of the Phenylhydrazides of certain Acids of the Sugar Group. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1917, **39**, 462—470).—Using Nef's figures (compare A., 1914, i, 490) for the specific rotatory powers of the phenylhydrazides of *d*-gluconic, *d*-gulonic, *d*-idonic, and *d*-galactonic acids, all of which contain α-, β-, γ-, and δ-asymmetric carbon atoms, the author calculates the rotation due to each of these atoms, and finds that the rotation due to the α-carbon atom is so very much larger than the values due to the other three atoms added together that the direction of rotation of the phenylhydrazide indicates the configuration of the hydroxyl group on the α-carbon atom. This is supported by the value for β-galaheptonic phenylhydrazide, the structure of which was settled by Peirce (compare A., 1916, i, 18). Further support is given by the specific rotatory powers of the phenylhydrazides of β-mannoheptonic acid (Peirce, *loc. cit.*), and of *d*-erythronic, *d*-threonic, and *d*-lyxonic acids (compare Nef, *loc. cit.*). In order to test the matter further, the author has prepared the following phenylhydrazides and measured their specific rotations in water: *d*-arabonic phenylhydrazide, $[\alpha]_D^{20}$ −14·5°; *d*-mannonic phenylhydrazide, $[\alpha]_D^{80}$ −8·1°; *l*-rhamnonic phenylhydrazide, $[\alpha]_D^{80}$ +17·2°; *d*-α-glucoheptonic phenylhydrazide, $[\alpha]_D^{20}$ +9·3°; *d*-α-mannoheptonic phenylhydrazide, $[\alpha]_D^{80}$ +21°; and *d*-α-galaheptonic phenylhydrazide, $[\alpha]_D^{80}$ +8·7°. The rule holds for these six phenylhydrazides.

W. G.

Preparation of Acetaldehyde. UNION CARBIDE Co. (U.S. Pats., (*A*) 1213486 and (*B*) 1213487; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—(*A*) Acetaldehyde is produced by passing acetylene into dilute sulphuric acid containing a mercury salt and a salt of a relatively weak acid which is not reduced under the working conditions, for example, a borate. The acetaldehyde may be distilled off simultaneously. (*B*) Acetaldehyde is produced by passing acetylene into a solution containing a mercury salt and an acid salt of a strong acid, for example, a bisulphate, but practically no hydrogen ions. The solution may also contain a salt of a relatively weak acid and the acetaldehyde may be distilled off simultaneously.

H. W.

The Sterical Relationships between Glyceraldehyde and Tartaric Acid. A. WOHL and FR. MOMBER (*Ber.*, 1917, **50**, 455—462).—Dextrorotatory glyceraldehyde (A., 1915, i, 216) has been converted by the hydrogen cyanide synthesis into a trihydroxybutyric acid which yields *l*-tartaric acid on oxidation. It has therefore the same configuration as dextrose, and the designation "*d*-glyceraldehyde" will fortunately express both its optical activity and spatial relationships.

Some difficulty was experienced at first in effecting the hydrogen cyanide condensation, starting with glyceraldehyde dimethylacetal (*ibid.*). Assuming that the free aldehyde was peculiarly resistant to this action, the dibenzoate and diacetate of the acetal were prepared in the hope of hydrolysing these to the esters of the free aldehyde, but it was found that such a partial hydrolysis could not be effected. *Diacetylglyceraldehyde dimethylacetal*,

$$OAc\cdot CH_2\cdot CH(OAc)\cdot CH(OMe)_2,$$

has b. p. 128—129°/14 mm. Finally, it was realised that glyceraldehyde dimethylacetal is not completely hydrolysed by $0·1N$-sulphuric acid in the cold, as was assumed. Warming for some time at 50° is necessary. *d*-Glyceraldehyde is now found to have a lower rotation than was originally stated, namely, $[\alpha]_D$ +13—14°.

After hydrolysing the acetal completely in this way, the addition of hydrogen cyanide can be effected in the presence of ammonia (HCN and NH_3, 1·5 mols. each). The nitrile may then be hydrolysed by barium hydroxide, and the brucine salt of the acid so formed may be obtained in clusters of needles, m. p. 204° (decomp.), $[\alpha]_D^{17}$ −29·9°. The salt is most probably a mixture of the salts of *l*-threonic and *d*-erythronic acids. The mixture of free acids may be oxidised by Fischer's method (A., 1896, i, 525) and the tartaric acid identified as the potassium salt.

Some useful suggestions are made for a simplification of the symbols for the aldoses. In reviewing the sterical relationships of the aldoses, it is only necessary, for example, to agree to consider the aldehyde group as being to the right of the formula and then to express in writing merely the groups on one side of the central chain, say, the lower side. Thus dextrose might be written OH OH H OH.

J. C. W.

Glyoxal. K. HESS and CL. UIBRIG (*Ber.*, 1917, **50**, 365—368).—Polymerised glyoxal can be depolymerised by boiling with anethole, phenetole, safrole, methyl nonyl ketone, benzaldehyde, and especially readily with acetic anhydride. With the last agent, it is observed that the solvent soon becomes greenish-yellow and that the vapour also contains monomeric glyoxal. After some hours, however, the solution becomes colourless again, and then *ethenyl tetra-acetate*, $C_2H_2(OAc)_4$, is deposited on cooling in cubes or rectangular prisms, m. p. 106—107°. This derivative of glyoxal is very reactive, and will undoubtedly serve in reactions involving the use of the dialdehyde. It reduces alkaline permanganate and ammoniacal silver oxide, and reacts with phenylhydrazine acetate

solution to form phenylglyoxalosazone, which crystallises in bundles of long, golden-yellow spikes from alcohol or reddish-brown prisms from 80% acetic acid, m. p. 169—170°. J. C. W.

The Forms of *d*-Glucose and their Mutarotation. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1917, **39**, 320—328).—The authors find that acetic acid of various concentrations is the most suitable solvent from which to crystallise glucose (compare Griffen and Nelson, A., 1915, i, 675). To prepare β-glucose from the purified glucose, 10 parts of the sugar are dissolved in 1 part of water on a water-bath, and to the solution 12 parts of glacial acetic acid heated to 100° are added. The whole is well mixed and removed from the water-bath, when crystallisation at once commences. After four such crystallisations, pure β-glucose is obtained. To obtain the α-form, 2 parts of the sugar are dissolved in 1 part of water and 4 parts of glacial acetic acid added, and the liquid set on one side for crystallisation to take place at the ordinary temperature.

The velocity coefficient, (k_1+k_2), at 25° of the mutarotation of β-glucose shows a slight increase with the concentration of the solution until a maximum rate is reached at 25 grams of the sugar in 100 c.c. of solution. In dilute solutions (under 10 grams in 100 c.c.), the rate is independent of the concentration.

The velocity coefficients for α- and β-glucose have been measured over a range of temperature from 0° to 40°, and are found to be the same for the two sugars at each temperature. They can be calculated from the formula $\log(k_1+k_2)=C-A/T$, where C and A are constants. For an increase of 10° in temperature the rate increases 2·8 times. The acceleration of the hydrogen-ion catalysis of the mutarotation with rising temperature is the same as the acceleration by increased temperature of the rate of mutarotation in pure water. W. G.

Trimethyl Glucose [Dextrose Trimethyl Ether] from Cellulose. WILLIAM SMITH DENHAM and HILDA WOODHOUSE (T., 1917, **111**, 244—249. Compare T., 1913, **103**, 1735; 1914, **105**, 2357).—The most characteristic of the methylated glucoses obtained by the hydrolysis of methylated cellulose (*loc. cit.*) is a trimethyl glucose, and the probable structure of this compound is now discussed more particularly in the light of the discovery of γ-glucose and its derivatives. From a comparison of the properties of the trimethyl glucose with those of γ-glucose derivatives (Irvine, Fyfe, and Hogg, T., 1915, **107**, 526), the conclusion is drawn that the former compound is not of the γ-glucose structure, but is to be regarded as derived from the butylene oxide structure. By a consideration of the various possible constitutions of the butylene oxide type for the trimethylglucose, and from the fact that by the cyanohydrin synthesis this substance is convertible into an acid which behaves as if partly lactonised, but which has in the process of lactonisation lost a

methyl group, the authors arrive at a decision that the structure of the trimethyl glucose is to be represented:

$$\left.\begin{matrix}\mathrm{CH(OH)}\text{———————}\mathrm{O} \\ \mathrm{CH(OMe)\cdot CH(OMe)}\end{matrix}\right\rangle \mathrm{CH\cdot CH(OH)\cdot CH_2\cdot OMe}.$$

A compound of this constitution would by the cyanohydrin synthesis give rise to an acid which could form a lactone only by demethylation. D. F. T.

The Preparation of Pure Crystalline Mannose and a Study of its Mutarotation. C. S. HUDSON and H. L. SAWYER (*J. Amer. Chem. Soc.*, 1917, **39**, 470—478).—A method is described for the preparation of crystalline β-mannose by the acid hydrolysis of vegetable ivory without the intermediate preparation of the phenylhydrazone (compare Fischer and Hirschberger, A., 1889, 480, 687). The vegetable ivory meal (150 grams) is slowly added in small quantities to a 75% solution of sulphuric acid (150 grams), the temperature not being allowed to rise above 40°. After twelve hours, the mixture is diluted with 2 litres of water and boiled for three hours under a reflux condenser. After cooling, the solution is neutralised with calcium hydroxide and filtered, and to the filtrate 0·5% of glacial acetic acid is added. The solution is decolorised with bone black, clarified with basic lead acetate solution, and the lead precipitated with hydrogen sulphide. The filtrate is evaporated to a thin syrup, diluted with alcohol, and filtered to remove calcium salts. Hydrogen sulphide is again passed through the alcoholic solution, which is finally filtered and evaporated to a viscous syrup, from which, on the addition of an equal volume of glacial acetic acid, β-mannose slowly crystallises. So prepared, it has D^{20} 1·539. The rate of mutarotation of this specimen in aqueous solution was measured at temperatures from 0° to 45°, and the reaction was found to be unimolecular (compare Pratolongo, *Rend. Inst. Lombardo*, 1912, **45**, 975), the increase in speed being 2·6 times for 10° rise in temperature. This rate of mutarotation is independent of the concentration for solutions less than 10% in strength. Above this, the rate increases with the concentration to a maximum, and then decreases. Hydrochloric acid acts as a catalyst for this reaction, the increase in rate being proportional to the increase in acidity within the range $N/1000$ to $N/10$. One drop of ammonium hydroxide brings about an equilibrium value for the rotation almost instantly. W. G.

Pectin Substances, their Constitution and Importance. FELIX EHRLICH (*Chem. Zeit.*, 1917, **41**, 197—200).—The author, as the result of the investigation of the pectin substances obtained from sugar beet, has isolated a new substance, which stands in the same relation to *d*-galactose as does *d*-glycuronic acid to *d*-glucose. This substance he has named *d*-galacturonic acid. The residual cell material remaining after the removal of sugar from the sugar beet was used to prepare raw pectin. This material is shown to be

a mixture of two easily separable substances. The one, present only in small quantity, is a lævorotatory arabin ($[\alpha]_D = -74°$ to $-121°$). The other is a calcium magnesium salt of pectic acid, which is a dextrorotatory ester acid. This substance can also be obtained from the skins of apricots and oranges. On treating the salt with alcohol and hydrochloric acid, the free pectic acid is obtained as a viscid, colourless jelly, which dries to a colourless powder. It is distinctly acid to litmus and phenolphthalein, dextrorotatory, $[\alpha]_D = +220°$, and contains 9% of methoxyl groups. It gives the orcinol and resorcinol reactions for pentose, but its oxidation with nitric acid yields mucic acid, thus showing that it does not contain pentoses, but galactose. On heating pectic acid with 1% oxalic acid, it is hydrolysed, and yields *galactosegalacturonic acid*, a monobasic acid of the formula $C_{12}H_{20}O_{12} = C_6H_{12}O_6 + C_6H_{10}O_7 - H_2O$. This substance is a white, amorphous powder easily soluble in water and in alcohol; it forms calcium and barium salts, which are also soluble in water, but sparingly so in alcohol. It gives the orcinol and naphtharesorcinol reactions, and on oxidation with nitric acid yields mucic acid. Complete hydrolysis of pectic acid into *d*-galactose and *d*-galacturonic acid is effected by heating with oxalic acid under 2—3 atmospheres pressure at 130—140°. Pure galacturonic acid cannot, however, be isolated from the products of hydrolysis. If, on the other hand, pectic acid is treated with excess of cold sodium hydroxide solution, a white, flaky precipitate is deposited in a few seconds. This substance is an amorphous, white powder, which is easily soluble in dilute alkalis, and from the solution it is precipitated by acids. It has a rotatory power $[\alpha]_D = +270°$, and is formed from pectic acid by the elimination of the methoxyl and galactose groups. The author regards it as being an anhydride of *d*-galacturonic acid, $4C_6H_{10}O_7 - 3H_2O = C_{24}H_{34}O_{25}$, formed in such a way that the separation of water takes place between the aldehyde and hydroxyl groups. This acid, d-*tetragalacturonic acid*, gives all the reactions of the pentoses and glycuronic acid, except that on oxidation it forms mucic acid and not saccharic acid. When heated for two hours under a pressure of 2—3 atmospheres with 1% oxalic acid solution, it breaks down into *d*-galacturonic acid. This substance has only been obtained as a syrup in alcohol or water; it is slightly dextrorotatory, and gives the orcinol, resorcinol, and phloroglucinol reactions. It reduces Fehling's solution cold, and on heating with hydrochloric acid it yields furfuraldehyde. It may be precipitated from solution by lead acetate, and with lime water or baryta water it yields basic salts. The normal calcium and barium salts are soluble in water or alcohol. It forms no crystallisable compounds with phenylhydrazine derivatives, and this serves to distinguish it from *d*-glycuronic acid. The cinchonine salt is the only crystalline derivative of this acid which has yet been obtained. This has the formula $C_6H_{10}O_7,C_{19}H_{22}ON_2$; it melts sharply at 158° and has $[\alpha]_D = +134°$. Galacturonic acid is readily oxidised by bromine water to mucic acid, a reaction which serves to identify it in the

presence of galactose. Pectin substances obtained from a large number of fruits and vegetables have all been shown to be derivatives of this acid, so that the author regards it as playing an important part in the structure of plant material. As a result of the whole investigation, he draws the conclusion that the pectin of the cell membranes of plants is a calcium–magnesium salt of a complex *anhydro-arabino-galactose-methoxy-tetragalacturonic acid.* As to the method of linking of the various groups, there is no evidence on which to base definite conclusions, except that the arabinose group is weakly held in the molecule, whereas the galactose group is firmly held. The rest of the paper deals with possible uses of pectin substances as foods. J. F. S.

Indirect Formation of Double Salts. VI. The Double Silver, Lead, Bismuth, Copper, and Mercurous Haloids of Substituted Ammonium Bases. RASIK LAL DATTA and JNANENDRA NATH SEN (*J. Amer. Chem. Soc.*, 1917, **39**, 750—759. Compare Datta and Ghosh, A., 1914, i, 729).—The salts described have been prepared by interaction of the metallic nitrate and the substituted ammonium haloid in concentrated aqueous solutions. In the case of the lower members of the substituted ammonium bromides, silver nitrate only gives a precipitate of silver bromide, the method failing even for tetramethyl- and tetraethyl-ammonium bromides. It is only the bromides of the heavy, heterocyclic bases that give double silver bromides. The following have been prepared, having the constitution XBr,AgBr:

Pyridine silver bromide, a white, crystalline solid, m. p. 151°, readily decomposed by water; *quinoline silver bromide,* white, crystalline solid, m. p. 180°; iso*quinoline silver bromide,* m. p. 127°; *a-picoline silver bromide,* m. p. 157°. All these melted to yellow liquids and were decomposed by water.

The following double lead haloids were prepared:

Tetraethylammonium lead iodide, $3NEt_4I,2PbI_2$, m. p. 212°; *tetrapropylammonium lead iodide,* NPr_4I,PbI_2, m. p. 194°; p-*tolyltrimethylammonium lead iodide,* $3NMe_3(C_7H_7)I,2PbI_2$, a bright yellow solid, turning black when heated; *ethylquinolinium lead iodide,* C_9H_7NEtI,PbI_2, m. p. 190°; *tetramethylammonium lead bromide,* $3NMe_4Br,2PbBr_2$; *tetraethylammonium lead bromide*; *pyridinium lead bromide,* $C_5H_5N,HBr,PbBr_2$, a white solid, turning yellow at 130°; *quinolinium lead bromide,*

$$C_9H_7N,HBr,PbBr_2,$$

decomposing at 320°; *a-picolinium lead bromide,*

$$C_5H_4NMe,HBr,PbBr_2,$$

m. p. 168—169°, to a viscid, black liquid; *pyridinium lead chloride,* $C_5H_5N,HCl,PbCl_2$; *a-picolinium lead chloride,*

$$C_5H_4NMe,HCl,PbCl_2;$$

quinolinium lead chloride, $C_9H_7N,HCl,PbCl_2$; *phenylbenzyldiethyl ammonium lead chloride,* $C_7H_7{\cdot}NEt_2PhCl,PbCl_2$.

Double bismuth haloids have been prepared as follows:

Tetraethylammonium bismuth iodide, NEt_4I,BiI_3; *tetrapropyl ammonium bismuth iodide,* NPr_4I,BiI_3; p-*tolyltrimethylammonium*

bismuth iodide, $C_7H_7{\cdot}NMe_3I,BiI_3$; *ethylquinolinium bismuth iodide*, C_9H_7NEtI,BiI_3; *tetramethylammonium bismuth bromide*; *tetraethylammonium bismuth bromide*; *pyridinium bismuth bromide*, a yellow solid, turning red suddenly at 210°; *quinolinium bismuth bromide*. These bromides have the general formula $2XBr,BiBr_3$. *Pyridinium bismuth chloride*, $2C_5H_5N,HCl,BiCl_3$, m. p. 245° (decomp.); *quinolinium bismuth chloride*,

$$2C_9H_7N,HCl,BiCl_3;$$

phenylbenzyldiethylammonium bismuth chloride,

$$C_7H_7{\cdot}NEt_2PhCl,BiCl_3.$$

For the preparation of the double cuprous haloids, a hydrochloric acid solution of cuprous chloride was used. *Tetrapropylammonium cuprous iodide*, NPr_4I,CuI; p-*tolyltrimethylammonium cuprous iodide*, $C_7H_7NMe_3I,CuI$; *quinolinium cuprous iodide*, C_9H_7N,HI,CuI; methylquinolinium cuprous iodide (compare Kohn, A., 1912, i, 801); *triethylsulphonium cuprous iodide*, SEt_3I,CuI; *tetramethylammonium cuprous bromide*,

$$NMe_4Br,2CuBr;$$

tetraethylammonium cuprous bromide, m. p. 130°; *phenylbenzyldiethylammonium cuprous bromide*, $C_7H_7NEt_2PhBr,CuBr$, a pale yellow, viscous oil, readily decomposing; *pyridinium cuprous bromide*, $C_5H_5N,HBr,CuBr$, unstable, yellow plates; *quinolinium cuprous bromide*, $C_9H_7N,HBr,CuBr$; iso*quinolinium cuprous bromide*; *a-picolinium cuprous bromide*, $C_5H_4NMe,HBr,CuBr$.

Double mercurous iodides were obtained with the heavily substituted ammonium bases. p-*Tolyltrimethylammonium mercurous iodide*, $C_7H_7{\cdot}NMe_3I,HgI$; *tetrapropylammonium mercurous iodide*, $2NPr_4I,HgI$. W. G.

Preparation of Salts of Hexamethylenetetraminemethylhydroxide. K. H. SCHMITZ (D.R.-P., 295736; from *J. Soc. Chem. Ind.*, 1917, **36**, 306).—Ammonia, formaldehyde, or one of its polymerides, and an acid or acid ion are heated for several hours and the product treated with a soluble dichromate; the resulting sparingly soluble chromate, $(C_6H_{12}N_4Me)_2Cr_2O_7$, is decomposed with barium hydroxide and the precipitated barium chromate filtered off. Alternatively, hexamethylenetetraminemethyl chloride, bromide, iodide, or thiocyanate is digested with silver oxide, the resulting solution of the free base is concentrated in a vacuum, neutralised by any desired inorganic or organic acid to form the corresponding salt, and the solution evaporated in a vacuum. The salts of this base have the property of liberating formaldehyde in alkaline solutions, which is not the case with hexamethylenetetramine salts, and have a therapeutic value. H. W.

Colloidal Ferric Ferricyanides. R. HALLER (*Kolloid Zeitsch.*, 1917, **20**, 76—81).—By the interaction of aqueous solutions of ferric chloride and potassium ferricyanide, colloidal ferric ferricyanide is formed. The freshly formed colloid is highly disperse, but ultramicroscopic observations show that the particles undergo a gradual process of aggregation, and this leads ultimately to the separation of Prussian green. By the action of sodium hyposulphite on the

brown colloidal solution, a mixture of colloidal Prussian blue and Turnbull's blue is obtained. Further reduction yields colloidal Prussian white.

The actual result of the action of potassium ferricyanide on ferric chloride varies with the concentration of the aqueous solutions. If alcoholic solutions of ferric chloride and potassium ferricyanide are mixed together, ferric ferricyanide is obtained in the form of an unstable, gelatinous precipitate. H. M. D.

The Preparation of Alkyloxyurea [Alkyloxyaminoformyl] Chlorides and their Relation to Esters of Carbon Dioxide Oxime, RO·N:C:O. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1917, **39**, 652—659. Compare A., 1898, i, 172).—When phosphorus pentachloride is added slowly to *α*-benzyloxyurethane, hydrogen chloride and ethyl chloride are evolved and at 50° a violent reaction occurs giving a dark brown liquid. This, when distilled under reduced pressure, gives benzylidene chloride, the course of the reaction probably being:

$$C_7H_7{\cdot}O{\cdot}NH{\cdot}CO_2Et \longrightarrow C_7H_7{\cdot}O{\cdot}NH{\cdot}COCl \longrightarrow C_7H_7O{\cdot}N{:}C{:}O,$$

the last compound decomposing or polymerising in part at 50°. *α-sec.*-Butoxyurethane under similar conditions gives *α*-sec.-*butoxylaminoformyl chloride*, a yellow oil, along with ethyl chloride and hydrogen chloride, the formation of the latter being due probably to the partial decomposition of the aminoformyl chloride (compare Gattermann and Schmidt, A., 1887, 358). sec.-*Butoxyethylaminoformyl chloride*, a clear, colourless liquid, b. p. 80°/25 mm., is similarly prepared from the corresponding hydroxyurethane. *Ethoxyethylaminoformyl chloride*, b. p. 74—76°/25 mm., is similarly obtained. In some cases these aminoformyl chlorides are decomposed in the presence of water into hydroxylamine derivatives and carbon dioxide.

When carbonyl chloride is passed over hydroxylammonium chloride, the temperature being gradually raised to 100°, a clear liquid is formed and begins to distil, but explodes violently. With *α*-ethoxylammonium chloride at 200°, a clear *liquid*, $C_3H_7O_2NCl_2$, b. p. 190—200°, is obtained, and with *α*-benzyloxylammonium chloride a clear *liquid*, $C_8H_9O_2NCl_2$, b. p. 97·5—100°/49 mm., is obtained. With hydroxylamine at 45° carbonyl chloride gives a *compound*, a white, crystalline solid, m. p. 79·5—81° (decomp.), which gives a purple coloration with ferric chloride, and a green *copper* salt with copper acetate. The compound probably has the composition HO·NH·COCl. With ethoxylamine, carbonyl chloride gives at low temperatures a mixture of ethoxylammonium chloride and a *compound*, $C_5H_{13}O_3N_2Cl$, a clear, colourless oil. W. G.

Hydroxamic Acids Related to *α*-Hydroxy-acids and to Acrylic Acid, and a Study of their Rearrangements. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1917, **39**, 659—668. Compare A., 1898, i, 172).—Some new hydroxamic acids have been prepared by the action of free

hydroxylamine on the esters of certain acids, and the behaviour of these hydroxamic acids under the influence of heat and hydrolysing agents has been studied.

Ethyl propionate with hydroxylamine in methyl alcohol gives propionhydroxamic acid, $CH_2Me\cdot CO\cdot NH\cdot OH$, m. p. 92·5—93° (compare Miolati, A., 1892, 698). The *copper*, *potassium*, *sodium*, *mercury*, *silver*, and *lead* salts are described. The free acid gives a *benzoyl* derivative, $CH_2Me\cdot CO\cdot NH\cdot O\cdot COPh$, slender needles, m. p. 115—116°, which in turn yields *sodium*, *potassium*, and *silver* salts. The benzoyl derivative, when heated in a sealed tube in a water-bath with aqueous potassium hydroxide, decomposes, giving potassium benzoate, and on acidifying the solution with hydrochloric acid, ethylammonium chloride is also obtained. Propionhydroxamic acid also yields an *acetyl* derivative, glistening plates, m. p. 72·5—73°, which forms *sodium*, *potassium*, and *silver* salts.

Lacthydroxamic acid, $HO\cdot CHMe\cdot CO\cdot NH\cdot OH$, a viscid, colourless oil, prepared as above, yields a *benzoyl* derivative, m. p. 124·5—126°, giving a *potassium* salt. The benzoyl derivative when heated with water on a water-bath for three hours gives carbon dioxide, ammonia, acetaldehyde, and *s*-dibenzoylcarbamide. *Mandelhydroxamic acid*, $HO\cdot CHPh\cdot CO\cdot NH\cdot OH$, m. p. 143·3°, gives a *benzoyl* derivative, m. p. 101—102°, which very readily decomposes in contact with water, giving benzaldehyde and *s*-dibenzoylcarbamide. *Acrylhydroxamic acid*,

$$CH_2{:}CH\cdot CO\cdot NH\cdot OH,$$

is a white, flaky solid, m. p. 115—116°. W. G.

Dichloroacethydroxamic Acid and its Rearrangement, and Aminoacethydroxamic Acid. LAUDER WILLIAM JONES and M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1917, **39**, 668—674).—When hydroxylamine in alcoholic solution is added to an alcoholic solution of ethyl dichloroacetate at −10°, *dichloroacethydroxamic acid*, $CHCl_2\cdot CO\cdot NH\cdot OH$, slender needles, m. p. 86—87°, is obtained. When heated at 145°, it is decomposed, giving carbon dioxide, hydrogen cyanide, hydrogen chloride, formic acid, ammonium chloride, dichloroacetamide, and dichloroacetic acid, the course of the decomposition being:

(1) $CHCl_2\cdot CO\cdot NH\cdot OH \longrightarrow CHCl_2\cdot CO\cdot N \longrightarrow CHCl_2\cdot N{:}C{:}O \longrightarrow CHCl_2\cdot NH_2 \longrightarrow HCN + 2HCl.$

(2) $CHCl_2\cdot CO\cdot NH\cdot OH \xrightarrow{H_2O} NH_2\cdot OH + CHCl_2\cdot CO_2H \xrightarrow{HCN} CHCl_2\cdot CO\cdot NH_2 + H\cdot CO_2H.$

(3) $NH_2\cdot OH + H\cdot CO_2H \longrightarrow CO_2 + NH_3 + H_2O.$

Further confirmation of this is obtained from the *benzoyl* derivative, b. p. 77—78°, which when heated decomposes, giving benzoic acid and a liquid having a sharp, carbimide-like odour, which when treated with water gives carbon dioxide, hydrogen chloride, and hydrogen cyanide. Attempts to prepare dichloromethylcarbimide by the interaction of sodium hydrazoate and dichloroacetyl

chloride only yielded an impure product, a colourless liquid, b. p. 85—90°, which had a sharp, penetrating odour, and was decomposed by water, giving carbon dioxide, hydrogen chloride, and hydrogen cyanide.

Ethyl trichloroacetate and hydroxylamine in alcoholic solution at −15° gave the *hydroxylammonium* salt of *trichloroacethydroxamic acid*, $CCl_3\cdot CO\cdot NH\cdot O\cdot NH_3\cdot OH$, m. p. 72—73°. Ethyl glycocollate and hydroxylamine gave *aminoacethydroxamic acid*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot OH$, m. p. 140° (decomp.). W. G.

The Thermal Decomposition of Benzene. J. E. Zanetti and G. Egloff (*J. Ind. Eng. Chem.*, 1917, **9**, 350—356).—A study of the thermal decomposition of benzene at temperatures varying from 500—800° at atmospheric pressure, the effect of varying the rate of flow of the benzene and the presence of catalysts being examined. The chief products of the decomposition are diphenyl, diphenylbenzenes, carbon, and a gas, no naphthalene being found in the decomposition products (compare Rittman, Byron, and Egloff, A., 1916, i, 132). The gas consisted of hydrogen saturated with benzene vapour, no acetylene being found. The formation of diphenyl begins at as low a temperature as 500°, the optimum temperature being 750°, above which diphenylbenzenes, as well as carbon and hydrogen, readily form. The slower rates of flow of the benzene are more favourable to the formation of diphenyl.

The catalysts examined were copper, iron, and nickel in the form of gauze. Iron and nickel favour the decomposition to carbon and hydrogen. Copper exerts no marked action except above 750°, when it accelerates the formation of carbon.

The thermal decomposition of benzene at atmospheric pressure takes place with the formation of condensation products, in which the benzene ring apparently remains intact, or with the complete breaking down to carbon and hydrogen without the formation of appreciable quantities of intermediate products, such as acetylene, ethylene, etc. W. G.

Halogenation. XV. Direct Iodination of Hydrocarbons by Means of Iodine and Nitric Acid. Rasik Lal Datta and Nihar Ranjan Chatterjee (*J. Amer. Chem. Soc.*, 1917, **39**, 435—441).—Iodine can be introduced directly into aromatic hydrocarbons by its action in the presence of nitric acid, the nitric acid being reduced to the lower oxides of nitrogen. In the case of the lower hydrocarbons, the chances of iodination are greater than those of nitration, but with the higher hydrocarbons the reverse is the case (compare Datta and Fernandes, A., 1916, i, 715). The nitric acid exerts to a small extent its hydrolysing influence, and with benzene a very small quantity of trinitrophenol can be isolated; but the nitric acid is added in small quantities, and thus its concentration is never sufficiently high for marked hydrolysis of the iodo-compound to occur. With the aliphatic hydrocarbons, however, the iodo-derivatives are hydrolysed as soon as they are

formed, but by careful working it is found possible to obtain small yields of the iodo-derivatives of some of the higher hydrocarbons. Using this method, benzene gave iodobenzene; toluene gave a mixture of *o*- and *p*-iodotoluenes; *o*-xylene gave 4-iodo-*o*-xylene; *m*-xylene gave 4-iodo-*m*-xylene; *p*-xylene gave 2-iodo-*p*-xylene; mesitylene gave iodomesitylene; ethylbenzene gave an iodoethylbenzene, b. p. 221—222°; cymene gave iodocymene; hexane gave a small yield of iodohexane; thiophen with dilute nitric acid and iodine in the cold gave iodothiophen; naphthalene gave a mixture of iodo- and nitro-naphthalene; anthracene did not yield an iodo-derivative, but was oxidised to anthraquinone. W. G.

The Action of Sulphuric Acid on Certain Nitrocarbocyclic Compounds. I. The Action on Nitrobenzene. M. L. Crossley and C. B. Ogilvie (*J. Amer. Chem. Soc.*, 1917, **39**, 117—122).—When nitrobenzene is heated with concentrated sulphuric acid at 195°, a vigorous action occurs, and from the product, after repeated extraction with boiling water, a black, melanin-like substance is obtained, which is practically insoluble in most organic solvents, but slightly soluble in pyridine, quinoline, and trimethylamine, giving reddish-purple solutions having a reddish-brown fluorescence. The aqueous extract on evaporation yields crystals of *p*-aminophenol-*o*-sulphonic acid; this gives an *anilide*, m. p. 98°, and on treatment with bromine in acetic acid solution, bromoanil, m. p. 300°.

When β-aminoanthraquinone, anthraquinone, or anthracene is separately added to the mixture of nitrobenzene and sulphuric acid, purplish-black reaction products are obtained which are similar to but not identical with the product obtained with nitrobenzene alone, but aminophenolsulphonic acid is not obtained. The black products in all cases dissolve in hot concentrated sodium hydroxide, and on the addition of sodium hyposulphite are reduced, giving dyes which dye cotton. The product from nitrobenzene dyes cotton a steel-grey. That from the aminoanthraquinone gives a brown vat, oxidising on cotton to a heliotrope. The anthraquinone product dyes cotton steel-grey, and the anthracene product dyes cotton brown. These dyes are not fast to boiling alkalis.
W. G.

The Reaction between Aromatic Sulphinic Acids and Di- and Tri-phenylcarbinols. O. Hinsberg (*Ber.*, 1917, **50**, 468—473).—When equivalent quantities of benzenesulphinic acid and *pp'*-tetramethyldiaminobenzhydrol are mixed in dilute hydrochloric acid solution, a compound is formed which is colourless in benzene or acetone and deep blue in acetic acid solutions. Originally this was supposed to have the formula

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3(NMe_2) \cdot SO_2Ph \text{ (meta)}$$

(A., 1898, i, 140). It is now shown, however, that it is *phenyl pp'-tetramethyldiaminodiphenylmethyl sulphone*,

$$(NMe_2 \cdot C_6H_4)_2CH \cdot SO_2Ph,$$

which exists in the quinonoid form, $NMe_2{\cdot}C_6H_4{\cdot}CH{:}C_6H_4{<}^{NMe_2}_{SO_2Ph}$, in the coloured solutions. The evidence is to the effect that changes in the compound brought about at the central carbon atom necessitate the displacement of the sulphone residue. Thus, on reduction with zinc and dilute acid, the products are tetramethyldiaminodiphenylmethane and phenyl mercaptan; boiling with methyl-alcoholic sodium hydroxide causes hydrolysis to the hydrol methyl ether, m. p. 73°, and benzenesulphinic acid, whilst on warming with dimethylaniline and acetic acid, leuco-crystal-violet is produced.

Other sulphinic acids and hydrols react in the same way. Thus, Michler's hydrol condenses with β-anthraquinonesulphinic acid to form *tetramethyldiaminodiphenylmethyl β-anthraquinonyl sulphone*, $C_{14}H_7O_2{\cdot}SO_2{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, which crystallises in brownish-red leaflets, m. p. 220°, and gives deep blue solutions in acetic acid. Benzhydrol reacts with α-naphthalenesulphinic acid to form *diphenylmethyl α-naphthyl sulphone*, colourless needles, m. p. 183°, and with benzenesulphinic acid to give *phenyl diphenylmethyl sulphone*, m. p. 187°.

Triphenylcarbinol and α-naphthalenesulphinic acid give a strange product, m. p. 162°, which is free from sulphur. J. C. W.

Diphenylbutadiene. J. M. Johlin (*J. Amer. Chem. Soc.*, 1917, **39**, 291—293).—The author considers that the hydrocarbon, $C_{16}H_{14}$, m. p. 49°, obtained from acetophenonepinacone by Thörner and Zincke (compare A., 1880, 646) by dehydration with acetic anhydride, is diphenylbutadiene. Three new methods are described for the preparation of acetophenonepinacone, namely: (1) reduction of acetophenone by magnesium in the presence of mercuric chloride; (2) conversion of diacetyl into its diphenylpinacone by means of magnesium phenyl bromide; (3) action of magnesium methyl iodide on benzil. Method (3) is the most convenient. W. G.

Normal Potassium Persulphate as a Reagent in Organic Chemistry. Rasik Lal Datta and Jnanendra Nath Sen (*J. Amer. Chem. Soc.*, 1917, **39**, 747—750. Compare Wolffenstein, A., 1904, i, 896).—With normal potassium persulphate, quinol is to a large extent oxidised in the cold to quinhydrone. Aniline gives a good yield of aniline-black. *o*-Toluidine gives a quantitative yield of *o*-toluidine-black. Acetanilide and benzanilide are oxidised to *p*-benzoquinone, the acid radicles being detached. Acetamide, propionamide, and butyramide are hydrolysed to the corresponding acids. Allyl alcohol is oxidised to acraldehyde and a viscous, oily substance, still under investigation. Benzamide does not give benzoic acid, but a complex acid, not yet characterised, is produced. Cinnamic acid, pinene, and limonene give yellow to brown products of high molecular weight. With the aromatic amines and diamines, various dyes are produced, which are being investigated. W. G.

Preparation of Diphenylamine. B. J. FLÜRSCHEIM (U.S. Pat., 1212928; from *J. Soc. Chem. Ind.*, 1917, **36**, 382).—Aniline is heated with ferric chloride, finely divided copper, and iodine.

H. W.

β-Benzylformhydroxamic Acid. LAUDER WILLIAM JONES and M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1917, **39**, 674—679). —A solution of β-benzylhydroxylamine in ethyl formate kept for fourteen days at the ordinary temperature yielded *β-benzylformhydroxamic acid*, $CHO\cdot N(C_7H_7)\cdot OH$, long needles, m. p. 49—50°, giving a greyish-blue *copper* salt. The acid, when digested for two hours on a water-bath with an excess of a solution of dry hydrogen chloride in glacial acetic acid, underwent intramolecular oxidation in two directions, giving, on the one hand, carbon dioxide and benzylamine, and on the other hand formamide and benzaldehyde:

$$CHO\cdot N(OH)\cdot CH_2Ph \begin{cases} \rightarrow O{:}C{:}N\cdot CH_2Ph \rightarrow CO_2 + C_6H_5\cdot CH_2\cdot NH_2 \\ \rightarrow O{:}CH\cdot N{:}CHPh \rightarrow O{:}CH\cdot NH_2 + C_6H_5\cdot CHO \end{cases}$$

When distilled with phosphoric oxide, the acid gave benzylcarbimide, which, with aniline, yielded phenylbenzylcarbamide. W. G.

Nitrosoarylhydroxylamines. V. Internally Complex Metallic Salts. OSKAR BAUDISCH and ROSE FÜRST (*Ber.*, 1917, **50**, 324—327. Compare A., 1916, i, 386, 387, 388, 389).—The metallic salts of nitrosophenylhydroxylamine (cupferron) and α- and β-nitrosonaphthylhydroxylamine exhibit many differences in solubility which might be turned to account in analytical practice. An account of some of these solubilities is given.

For the preparation of the new β-naphthyl compound, β-nitronaphthalene is reduced by means of ammonium sulphide to *β-naphthylhydroxylamine*, silvery leaflets, m. p. 126°, and this is treated in ethereal solution with amyl nitrite in the presence of ammonia, when the *ammonium* salt, $C_{10}H_7\cdot N(NO)\cdot ONH_4$, separates in pearly leaflets, m. p. 159—160°. Free *β-nitrosonaphthylhydroxylamine* is obtained from this salt by means of metaphosphoric acid, in white needles, m. p. 88—92°. It is much more stable than the α-naphthyl compound (A., 1913, ii, 39), and gives precipitates with the merest traces of calcium or magnesium salts. The *copper* salt is pale bluish-green and the *ferric* salt is yellowish-brown.

If wool is steeped in a solution of ammonium β-nitrosonaphthylhydroxylamine and then exposed to a light, it becomes deep red, owing to the formation of α-hydroxy-β-azonaphthalene, which can be extracted from the wool by means of boiling alcohol and obtained in ruby-red needles, m. p. 234°. J. C. W.

Nitrosoarylhydroxylamines. VI. Internally Complex Metallic Salts. OSKAR BAUDISCH and NIKOLAUS KARZEFF (*Ber.*, 1917, **50**, 328—330).—For comparison with *o*-nitrosohydroxylamino-

phenol and its *p*-toluenesulphonate, the corresponding derivatives of *p*-nitrosophenol have been prepared (see A., 1912, i, 441).

p-Nitrophenyl *p*-toluenesulphonate is reduced by means of ammonium sulphide to p-*hydroxylaminophenyl* p-*toluenesulphonate*, m. p. 104·3°, and this is converted into p-*nitrosohydroxylaminophenyl* p-*toluenesulphonate*, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}N(NO){\cdot}OH$, white needles, m. p. 84·2°. Like the ortho-compound, this acid forms typical, internally-complex salts which are readily soluble in organic media, but differ from the salts of the ortho-acid in being soluble in an excess of hydrochloric acid. The *ammonium* salt, m. p. 132°, is precipitated when amyl nitrite is added to the above hydroxylamino-compound in ether saturated with ammonia; the *ferric* salt crystallises from ether in brown needles.

The ammonium salt can be hydrolysed by silver oxide to p-*nitrosophenyl* p-*toluenesulphonate*, which, unlike the ortho-compound, exists in only one form, white needles, m. p. 143°. The same salt is hydrolysed by sodium hydroxide, on the other hand, to *nitroso*-p-*hydroxyphenylhydroxylamine*, $OH{\cdot}C_6H_4{\cdot}N(NO){\cdot}OH$, which crystallises in leaflets, decomp. 70—100°, and forms a white *ammonium* salt, m. p. 131—132°. J. C. W.

Nitrosoarylhydroxylamines. VII. Internally Complex Metallic Salts. Note on Mordant Dyes. OSKAR BAUDISCH and FRANZ KLAUS (*Ber.*, 1917, **50**, 330—331).—*m*-Nitrophenol has been converted by the usual methods into the *ammonium* salt of *nitroso*-m-*hydroxyphenylhydroxylamine*, and the solubilities of the copper and cobalt salts of this acid have been compared with those of the salts of the corresponding *o*-hydroxy- and *p*-hydroxy-acids (A., 1912, i, 441, and preceding abstract). The salts in the ortho-series are very soluble in water, organic solvents, ammonia, or pyridine, and readily lose H and NO, whilst the salts in the para-series are insoluble except in ammonia or pyridine and are stable. The salts of the meta-acid take an intermediate position.

This influence of substituents on internally-complex groups is akin to the influence of substituents in *o*-hydroxyazo-compounds on their value as mordant dyes. J. C. W.

Preparation of Phenol and Other Substances. J. W. AYLSWORTH, A. M. AYLSWORTH, and THE SAVINGS, INVESTMENTS, AND TRUSTS CO., EXORS. (U.S. Pat., 1213142; from *J. Soc. Chem. Ind.*, 1917, **36**, 382).—Phenol is obtained by heating a mixture of chlorobenzene and alkali hydroxide solution, under pressure higher than that of the vapour tension of the mixture, at about 300°. Chloride and phenoxide are produced, and phenol is liberated from the latter by the action of acid. Where sodium hydroxide is used, the proportions are approximately: chlorobenzene (1 mol.), alkali hydroxide (2—3 mols.), and water (20 mols.).

H. W.

Electrolytic Oxidation of Cresols [Preparation of Salicylic Acid]. U. POMILIO (Brit. Pat., 103709; from *J. Soc. Chem. Ind.*, 1917, **36**, 382).—In the oxidation of cresols for the production of the corresponding hydroxy-acids or their salts, an electric current of 5—8 amperes per sq. dcm. is passed through a fused mixture of the cresol and alkali hydroxide at 200—270°, using electrodes of nickel, nickel-steel, iron, etc. For example, in the production of salicylic acid, a mixture of sodium hydroxide (3—5 parts) and water (1 part) at 110—120° is treated with *o*-cresol (85—95%, 1 part), added in small quantities at a time; the mixture is then heated at 240—250° and a current of 5—8 amperes per sq. dcm. at the anode passed through. H. W.

Halogenation. XVI. Iodination by Means of Nitrogen Iodide or by Means of Iodine in the Presence of Ammonia. RASIK LAL DATTA and NOGENDRA PROSAD (*J. Amer. Chem. Soc.*, 1917, **39**, 441—456).—It is found that the phenols and the nitrophenols can be satisfactorily iodinated by means of nitrogen iodide or by a solution of iodine in potassium iodide in conjunction with strong ammonium hydroxide solution. With the latter reagent the iodonitrophenols, as formed, give ammonium salts of varying degree of stability, which cannot be prepared once the iodonitrophenol has been isolated. In all cases the yields were quantitative. Phenol gave tri-iodophenol; *o*-cresol gave di-iodo-*o*-cresol; *m*-cresol gave tri-iodo-*m*-cresol; *p*-cresol gave 3:5-di-iodo-*p*-cresol; thymol gave 6-iodothymol; and *p*-5-xylenol gave a *monoiodo*-derivative which was not characterised. *o*-Nitrophenol gave the *ammonium* salt, m. p. 210° (decomp.), of 2:4-di-iodo-6-nitrophenol; *m*-nitrophenol gave the unstable *ammonium* salt, m. p. 165—170°, of 2-iodo-3-nitrophenol; *p*-nitrophenol gave 2:6-di-iodo-4-nitrophenol, no ammonium salt being isolated; 3-nitro-*p*-cresol gave *5-iodo-3-nitro-*p*-cresol*, yellow needles, m. p. 83·5°, isolated first as its *ammonium* salt, orange-red needles, m. p. 195—200°; phenolphthalein gave tetraiodophenolphthalein.

The phenolic acids could be less readily iodinated by iodine and ammonia than the phenols and nitrophenols, as, in addition to iodo- or di-iodo-derivatives, secondary products of a complex character were always formed. Salicylic acid gave 5-iodosalicylic acid and a pink *compound*; *m*-hydroxybenzoic acid gave 6-iodo-*m*-hydroxybenzoic acid; *p*-hydroxybenzoic acid gave 3:5-di-iodo-*p*-hydroxybenzoic acid and a compound not yet characterised; *p*-hydroxyphenylarsinic acid gave an *iodo*-derivative, $HO\cdot C_6H_3I\cdot AsO(OH)_2$, needles, m. p. 158°, which when boiled with water gave a pink *compound*, m. p. 230—240°.

Dimethylpyrone in the presence of iodine and ammonia gave a shining, micaceous substance, which was ultimately converted into *di-iodolutidone*, $CO{<}{\substack{CI:CMe\\CI:CMe}}{>}NH$, m. p. 230—235°, giving a *hydrochloride*, yellow needles, and iodoform. Pyrrole gave a quantitative yield of tetraiodopyrrole, and on this is based a simple

volumetric method for the estmation of pyrrole, using an $N/2$-solution of iodine in potassium iodide.

Acetylene acting on nitrogen iodide under water gives a quantitative yield of tetraiodoethylene, whilst phenylacetylene under similar conditions gives tri-iodostyrene, m. p. 108°.

In two cases nitrogen iodide acted as an oxidising agent as with quinol it gave quinhydrone, and with benzaldehyde it gave benzoic acid.

Iodoform is formed as a product of the systematic action of nitrogen iodide on the ketones (compare Chattaway, T., 1913, **103**, 1986), but if the reaction is carried out in concentrated solutions and at lower temperatures iodoketones are apparently formed, although none have yet been isolated. Thus acetone, methyl ethyl ketone, diethyl ketone, acetylacetone, acetylmethyl propyl ketone, acetylmethyl hexyl ketone, acetoxime, acetophenoneoxime, malonic ester, and acetoacetic ester all gave iodoform in the presence of nitrogen iodide, although with the first five there were strong indications of the formation of iodo-ketones. Diethylamine and triethylamine also gave iodoform with iodine and ammonia, as also did mesityl oxide. Iodine in the presence of ammonia has no action on ethyl and propyl alcohols. W. G.

The Identification of Phenols. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 304—309).—It is found that *p*-nitrobenzyl bromide readily reacts with the sodium or potassium phenoxides, giving ethers that are generally crystalline solids, and can be used as a means of identifying the phenols. The reaction is carried out in alcoholic solution, the mixture being heated on a water-bath under a reflux for one hour. The following ethers were prepared: Phenyl *p*-nitrobenzyl ether, m. p. 91° (compare Kumpf, A., 1884, 1005); o-*tolyl* p-*nitrobenzyl ether*, $C_6H_4Me\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2$, m. p. 89·7°; m-*tolyl* p-*nitrobenzyl ether*, m. p. 51°; p-*tolyl* p-*nitrobenzyl ether*, m. p. 88°; *thymyl* p-*nitrobenzyl ether*,

$$C_3H_7\cdot C_6H_3Me\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

m. p. 85·5°; *eugenyl* p-*nitrobenzyl ether*,

$$C_3H_5\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

m. p. 53·6°; and *vanillyl* p-*nitrobenzyl ether*,

$$CHO\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

m. p. 124·5°. All these ethers can be crystallised from alcohol.

W. G.

The Identification of Acids. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 124—136).—*p*-Nitrobenzyl bromide is a convenient reagent for the identification of acids. It readily forms esters of the acids when boiled in dilute alcoholic solution with the alkali salts of the acids. The esters can, in most cases, be readily purified by crystallisation from dilute alcohol. The following esters have been prepared:

p-*Nitrobenzyl formate*, m. p. 31°; acetate, m. p. 78° (compare Wachendorf, A., 1877, i, 207); *propionate*, m. p. 31°; *butyrate*, m. p. 35°; *benzoate*, m. p. 89°; o-*toluate*, m. p. 90·7°; o-*nitro-*

benzoate, m. p. 111·8°; o-*chlorobenzoate*, m. p. 106°; *anthranilate*, m. p. 205—210° (decomp.); p-*bromobenzoate*, m. p. 139·5°; 2:4-*dinitrobenzoate*, m. p. 142°; *phenylpropiolate*, m. p. 83°; thiocyanate, m. p. 85° (compare Henry, *Ber.*, 1869, **2**, 638); oxalate, m. p. 204° (compare Beilstein and Kuhlberg, *Annalen*, 1868, **147**, 340); *malonate*, m. p. 85·5°; *tartrate*, m. p. 163°; *citrate*, m. p. 102°.

Esters were made from salts of *iso*butyric, *iso*valeric, octoic, lactic, and α-hydroxybutyric acids, but the products were all oils which could not be induced to solidify. Attempts to prepare *p*-nitrobenzyl nitrite from potassium nitrite only gave a very small yield of a compound having a high melting point, and this was not proceeded with. With benzoic acid and its substitution products the yields are practically quantitative. The lower aliphatic monobasic acids also give good yields, but the yields from the polybasic acids are poor. W. G.

The Identification of Acids. II. J. A. LYMAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 701—711. Compare preceding abstract).—*p*-Nitrobenzyl esters of a number of other acids have been prepared, *p*-nitrobenzyl chloride and iodide being used in some cases in place of the bromide. With the dibasic acids, attempts to prepare the mono- as well as the di-ester failed in all cases except one, namely, malic acid. The following esters are described: p-*nitrobenzyl phenylacetate*, m. p. 65°; *cinnamate*, m. p. 116·7°; *β-phenylpropioante*, m. p. 36·3°; *hippurate*, m. p. 136°; m-*toluate*, m. p. 86·6°; *salicylate*, m. p. 96·3°; m-*hydroxybenzoate*, m. p. 106·1°; p-*hydroxybenzoate*, m. p. 198·5°; m-*aminobenzoate*, m. p. 198·3°; p-*aminobenzoate*, m. p. above 250°; *ethylmalonate*, $CHEt(CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, m. p. 75·2°; *dimethylmalonate*, m. p. 83·6°; *methylethylmalonate*, m. p. 65·6°; iso*propylmalonate*, m. p. 81·4°; *diethylmalonate*, m. p. 91·2°; *allylmalonate*, m. p. 46°; *dipropylmalonate*, m. p. 118·5°; *benzylmalonate*, m. p. 119·5°; *succinate*, m. p. 88·4°; *bromosuccinate*, m. p. 147·1°; *dibromosuccinate*, m. p. 168·5°; *maleate*, m. p. 89·3°; *fumarate*, m. p. 150·8°; *sebacate*, m. p. 72·6°; *malates*,

$$CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

m. p. 87·2°, and $C_2H_4O(CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, m. p. 124·5°; *racemate*, m. p. 147·6°; *phthalate*, m. p. 155·5°; iso*phthalate*, m. p. above 250°. The esters described above from dibasic acids are always the normal esters, except in the case of the malates. Esters could not be obtained with lævulic and mucic acids. W. G.

The Transformation of Nitriles into Amides by Hydrogen Peroxide. L. MCMASTER and F. B. LANGRECK (*J. Amer. Chem. Soc.*, 1917, **39**, 103—109. Compare Dubsky, A., 1916, i, 550).—By the action of hydrogen peroxide in a slightly alkaline medium, nine amides have been prepared in a pure state and with good yields from the corresponding nitriles. The amides thus prepared are benzamide, *m*-nitrobenzamide, *o*-toluamide, *p*-toluamide, α-naphthoamide, β-naphthoamide, terephthalamide, trichloroacetamide, and *iso*hexoamide. The authors have used more concen-

trated solutions of hydrogen peroxide than are usually employed, using in some cases a 20% solution, and thus succeeded in hydrolysing certain nitriles which had previously resisted the action of hydrogen peroxide (compare Deinert, A., 1896, i, 149). W. G.

Isomerisation, by Migration of the Double Linking, in the Ethylenic Acids. Phenyl-Δ^{α}-crotonic Acid, $CH_2Ph \cdot CH \colon CH \cdot CO_2H$. J. BOUGAULT (*Compt. rend.*, 1917, **164**, 633—636. Compare A., 1911, i, 202).—Phenyl-Δ^{α}-crotonic acid can be readily prepared from the liquid acid obtained in the reduction of α-iodophenylcrotonic acid with zinc and acetic acid (compare A., 1916, i, 817) by simply heating it with dilute hydrochloric acid. This Δ^{α}-acid is almost completely converted into its Δ^{β}-isomeride by warming it on a water-bath for three hours with dilute aqueous sodium hydroxide. The direction of this isomerisation is considered to be due to the presence of the electronegative phenyl group (compare Charon, *Rev. gen. des Sci.*, 1904, **15**, 447). W. G.

The Relationships between Keto- and Enol Forms in the Case in which the Enolisation is caused by a Positive β-Influence. L. RÜGHEIMER (*Ber.*, 1917, **50**, 396—401).—The question of the equilibrium between the two forms of ethyl β-benzyliminobutyrate has been investigated (compare A., 1916, i, 383).

The purest ketonic modification, $CH_2Ph \cdot N \colon CMe \cdot CH_2 \cdot CO_2Et$, obtained so far was prepared by the addition of benzylamine to an ethereal solution of ethyl acetoacetate at $-5°$, followed by crystallisation from cold ether, in which the enol is freely soluble. It forms elongated tablets, and in a bath previously warmed to 75° melts at 88·5—94·5°. The purest enolic modification, $CH_2Ph \cdot N \colon CMe \cdot CH \colon C(OH) \cdot OEt$, is obtained by distilling the compound under reduced pressure (b. p. 189°/20 mm.) and collecting the product in the dark. A fresh specimen has m. p. 19—22°, although the fusion is still somewhat turbid at 25°.

The ketonic form is permanent at the ordinary temperature if protected from catalytic influences, for example, from dust, but if heated, it suffers partial change into the enol, the m. p. becoming lower after each fusion. Conversely, the enol changes partly into the ketone at 20—23°, even in the dark, and therefore a fresh distillate is found to be solid after keeping for a few days.

It is thus established that equilibrium exists between the two forms in the liquid state. At higher temperatures the enolic form is favoured, whilst at lower temperatures the ketonic form is more stable, and in consequence of its small solubility a very complete transformation may take place. At about 53° it is possible to maintain both forms, liquid enol and solid ketone, together for some time. J. C. W.

The Action of the Tolylthiocarbimides on Sodiophenylacetylene. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1917, **39**, 697—701).—The tolylthiocarbimides condense with sodiophenyl-

acetylene, yielding on addition of acid thiotoluidides. Sodiophenylacetylene and *p*-tolylthiocarbimide react in ethereal solution to form *thiophenylpropiol*-p-*toluidide*, CPh:C·CS·NH·C_6H_4Me, yellow needles, m. p. 111—113° (decomp.), giving a *sodium* salt, colourless needles, which is unstable in water. The thiotoluidide when heated in ethereal solution with a few drops of aqueous sodium hydroxide polymerises, giving *bis-thiophenylpropiol*-p-*toluidide*, red plates, softening at 200°, but having no definite melting point. With phenylhydrazine in alcoholic solution the thiotoluidide, m. p. 111—113°, gives off hydrogen sulphide, and a brick-red precipitate is formed, but no crystalline product could be isolated (compare Moureu and Brachin, A., 1903, i, 581; 1904, i, 95). With hydroxylamine the thiotoluidide gives 3-p-*toluidino*-5-*phenyl*iso*oxazole*, white plates, m. p. 141·5°, hydrogen sulphide being evolved.

Thiophenylpropiol-m-*toluidide*, yellow needles, m. p. 118—120° (decomp.), was only obtained in small quantities, but qualitative tests indicate that it reacts with phenylhydrazine and with hydroxylamine, hydrogen sulphide being liberated.

Thiophenylpropiol-o-*toluidide* could only be obtained as a dark-coloured oil, giving a *sodium* salt, colourless plates. W. G.

Nitration of Isomeric Acetylaminomethoxybenzoic Acids. JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1917, **111**, 220—236. Compare Gibson, Simonsen, and Rau, this vol., i, 203). —An extension of the earlier nitration experiments to the simpler acids—3-acetylamino-2-methoxybenzoic acid, 5-acetylamino-2-methoxybenzoic acid, 4-acetylamino-3-methoxybenzoic acid, and 3-acetylamino-4-methoxybenzoic acid. The previous observation that the directing influence of a methoxy-group is much intensified by the juxtaposition of the acetylamino-group, in contrast with the opposite effect of a negative group, such as carboxyl, is, on the whole, borne out by the new results.

3-*Acetylamino*-2-*methoxybenzoic acid*, prepared through its parent *amino*-compound from 3-nitro-2-methoxybenzoic acid, when nitrated yielded the 4-*nitro*-, 5-*nitro*-, and 6-*nitro*-derivatives to the extent of 10, 42·8, and 40% respectively; the last-named product was further converted into 6-*nitro*-2-*methoxybenzoic acid* by the diazo-reaction.

5-*Acetylamino*-2-*methoxybenzoic acid*, obtained similarly from 5-*nitro*-2-*methoxybenzoic acid*, yielded the 4-*nitro*-, 6-*nitro*-, and 3-*nitro*-derivatives to the extent of 68, 7, and 22% respectively; 4-*nitro*-2-*methoxybenzoic acid* was obtained from the first of these products by diazotisation.

4-*Acetylamino*-3-*methoxybenzoic acid*, prepared in a similar manner to its isomerides, yielded its 6-*nitro*-derivative as the only simple nitration product.

3-*Acetylamino*-4-*methoxybenzoic acid*, prepared in the general manner, gave its 6-*nitro*-derivative as the only simple nitration product; this, by hydrolysis and diazotisation, was converted into 2-*nitro*-4-*methoxybenzoic acid*.

For experimental details and the description of the various compounds obtained in the preparation and nitration of the acetylamino-acids the original should be consulted. D. F. T.

Alkyl Ethers of Benzaldehydecyanohydrin. I. K. HESS and K. DORNER (*Ber.*, 1917, **50**, 390—394).—Alkyl ethers of benzaldehydecyanohydrin have not hitherto been described, although they are constitutionally related to amygdalin. A method for the preparation of such ethers has now been developed, which is indicated in the following scheme:

$$CHPhCl\cdot CO_2H \xrightarrow{NaOR} OR\cdot CHPh\cdot CO_2H \longrightarrow OR\cdot CHPh\cdot CO\cdot NH_2 \longrightarrow OR\cdot CHPh\cdot CN.$$

The methyl and ethyl compounds are described in this communication.

α-Chlorophenylacetic acid is boiled with sodium methoxide solution and so converted into α-methoxyphenylacetic acid, m. p. 70—71°, which is accompanied by a troublesome by-product, m. p. 91°, thus rendering this method less suitable than the usual one for obtaining the ether of mandelic acid. *α-Methoxyphenylacetyl chloride* has b. p. 119—121°/26 mm., and the *amide* crystallises in pearly plates, m. p. 112—114°, being best obtained from the methyl ester. *α-Methoxyphenylacetonitrile*, OMe·CHPh·CN, is obtained by heating the amide with pure thionyl chloride. It is a very stable, refractive, mobile oil, b. p. 116—118°/14 mm.

α-Ethoxyphenylacetamide forms pearly needles, m. p. 93—94°, and *α-ethoxyphenylacetonitrile* has b. p. 122—124°/16 mm. *Methyl α-ethoxyphenylacetate* has b. p. 127—129°/14—15 mm. J. C. W.

The Synthesis of Aryl-substituted Fatty Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1917, [ii], **95**, 55—62. Compare A., 1910, i, 115).—The author has extended to other aldehydes his method for the preparation of arylacetic acids.

[With (FRL.) ELSA MIKA.]—α-Naphthaldehyde was, in the general manner, converted into the corresponding *azlactone*, $C_{20}H_{13}O_2N$, yellow needles, m. p. 170—171°, by heating with hippuric acid, acetic anhydride, and sodium acetate; this product, on successive hydrolysis with sodium hydroxide solution and oxidation of the resulting alkaline solution with hydrogen peroxide, yielded α-naphthylacetic acid.

In an analogous manner, 2-methoxy-1-naphthaldehyde was converted into the *azlactone*, $C_{21}H_{15}O_3N$, yellow needles, m. p. 178—179°, which on hydrolysis with sodium hydroxide solution followed by prolonged distillation with steam gave 2-methoxy-1-methylnaphthalene and 2-*methoxy*-1-*naphthylpyruvic acid*, $C_{14}H_{12}O_4$, m. p. 119—120°; oxidation of the latter in acetic acid solution with hydrogen peroxide produced 2-*methoxy*-1-*naphthylacetic acid*, $C_{13}H_{12}O_3$, m. p. 210—211°. Similarly, 4-methoxy-1-naphthaldehyde yielded an *azlactone*, $C_{21}H_{15}O_3N$, reddish-yellow needles, m. p. 189—190°, which by hydrolysis and subsequent oxidation of the resulting alkaline solution was converted into 4-*methoxy*-1-*naphthylacetic acid*, $C_{13}H_{12}O_3$, colourless needles, m. p. 144—145°.

By the same general reaction *o*-chlorobenzaldehyde and *m*-bromobenzaldehyde were made to yield the corresponding *azlactones*, $C_{16}H_{10}O_2NCl$, yellow needles, m. p. 158—159°, and $C_{16}H_{10}O_2NBr$, m. p. 156—157° respectively, which were further convertible into *o*-chlorophenylacetic acid and *m*-bromophenylacetic acid respectively.

D. F. T.

The Salts of Phthalic Acid. JOHN B. EKELEY and CLIFFORD BANTA (*J. Amer. Chem. Soc.*, 1917, **39**, 759—768).—A study of the effect of heat on calcium phthalate under varying conditions of temperature and pressure, and an account of the preparation of a number of new salts of phthalic acid.

Calcium phthalate when heated either under reduced pressure at low temperatures, or at higher temperatures under pressure, only gave traces of anthraquinone (compare Panaotovic, A., 1884, 1039). The main products were resinous matter, phthalic anhydride, and benzophenone. Sodium phthalate when heated at 80° under a pressure of 13 mm. gave benzophenone as its principal product. Lead phthalate gave off water and carbon dioxide, leaving finely divided metallic lead.

The following new salts were prepared: *lithium*, $C_8H_4O_4Li_2$; *glucinum*, $C_8H_4O_4Gl,H_2O$; *manganese*, $C_8H_4O_4Mn$; *basic ferric*, $C_8H_4O_4(OH)Fe,2H_2O$; *cobalt*, $C_8H_4O_4Co,2H_2O$; *nickel*, $C_8H_4O_4Ni,2H_2O$; *cerium hydrogen*, $(C_8H_5O_4)_3Ce$; *mercuric*, $C_8H_4O_4Hg,H_2O$; *mercurous*, $C_8H_4O_4Hg_2,2H_2O$; *thorium*, $(C_8H_4O_4)_2Th,5H_2O$; *uranyl*, $UO_2{\cdot}C_8H_4O_4,2H_2O$.

W. G.

Diphenyltetrachlorophthalide and some of its Derivatives. W. R. ORNDORFF and (MISS) R. R. MURRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 293—304).—Tetrachlorophthalyl chloride, m. p. 118° (compare Graebe, A., 1887, 832) condenses with benzene in the presence of aluminium chloride, giving *diphenyltetrachlorophthalide*, $C_6Cl_4{<}\begin{matrix}CPh_2\\CO\end{matrix}{>}O$, thick needles, m. p. 250°. This phthalide is, however, better prepared by condensing the *acetate*, white prisms, m. p. 200°, of *o*-benzoyltetrachlorobenzoic acid, with benzene in the presence of aluminium chloride. If the acetate is condensed with toluene instead of benzene, it yields *phenyltolyltetrachlorophthalide*, pale yellow needles, m. p. 201°. If tetrachlorophthalyl chloride is condensed with toluene under similar conditions, *ditolyltetrachlorophthalide*, yellow plates, m. p. 209°, is obtained. All these tetrachlorophthalides resemble one another and diphenylphthalide in their properties.

When diphenyltetrachlorophthalide is nitrated in the cold with nitric acid (D 1·52) a mixture of two *dinitro*-derivatives is obtained, of which the isomeride less soluble in benzene, having m. p. 238—240°, is formed to the lesser amount, whilst the more soluble isomeride, m. p. 162—164°, is the principal product. Traces of a

third *dinitro*-compound, m. p. 180—185°, were found. Attempts to prepare the corresponding diamino-compounds were not successful, using stannous chloride and hydrochloric acid. Reduction took place, but the product contained tin, which could not be removed.

[With H. C. ALLEN.]—*o*-Benzoyltetrachlorobenzoic acid when condensed with phenol in the presence of stannous chloride yields *hydroxydiphenyltetrachlorophthalide*, colourless prisms, m. p. 268—270°, which may also be obtained by simply heating the acetate of *o*-benzoyltetrachlorobenzoic acid and phenol together at 180—190° for three hours. It gives an *acetate*, m. p. 211°.

Phenylresorcinoltetrachlorophthalein, m. p. 283—285°, was prepared by heating resorcinol and *o*-benzoyltetrachlorobenzoic acid acetate together at 160° for two hours. It crystallises from alcohol with 1EtOH and $1H_2O$ and from benzene with $1C_6H_6$. It yields a *diacetate*, silky, white needles, m. p. 235°. W. G.

A New Class of Phthaleins (mixed Phthaleins) formed by Heating *o*-4-Hydroxybenzoylbenzoic Acid with Phenols. W. R. ORNDORFF and (MISS) R. R. MURRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 679—697).—Phenolphthaleinoxime (compare Friedlander, A., 1893, i, 719) is obtained pure if less hydroxylamine hydrochloride, 12·5 instead of 15 grams, is used than recommended (*loc. cit.*). When boiled with dilute sulphuric acid, it is decomposed quantitatively, giving *o*-4-hydroxybenzoylbenzoic acid and *p*-aminophenol. The acid gives a *diacetate*, m. p. 137—140°, and when heated at 200—204° for two hours, an *anhydride*, m. p. 199—201°. When heated with various phenols, *o*-4-hydroxybenzoylbenzoic acid gave the corresponding phthalein. Thus with phenol itself a quantitative yield of phenolphthalein was obtained, no isomeric compound being formed. When heated with aniline, *o*-4-hydroxybenzoylbenzoic acid gave *phenolanilinephthaleinanilide*, colourless needles, m. p. 252—256°. It dissolves in boiling alkalis, giving a bluish-red solution of the alkali salt of the phenolanilinephthalein. Resorcinol gives two, isomeric, *phenolresorcinolphthaleins*, $C_{20}H_{14}O_5$, one crystallising in slender, white needles, m. p. 200—202°, the other in thicker needles or plates, m. p. 270—272°. If the crude product from this preparation is boiled with acetic anhydride for several hours, a mixture of the *mono*- and *di-acetates* is obtained, which, when boiled with sodium acetate and acetic anhydride, gives a mixture of the *triacetates* of the two phthaleins. These acetates are hydrolysed by boiling alcoholic alkali. *α-Naphtholphenolphthalein* could only be obtained as brown flocks, m. p. 110—130°, giving a light, yellowish-brown *diacetate*, m. p. 188—190°. *β-Naphtholphenolphthalein* was obtained as brown flocks and could not be purified, neither could its *acetate*. With *o*- and *p*-cresol, phthaleins were obtained which could not be purified.

When tetrachlorophthalic anhydride is condensed with anisole in the presence of aluminium chloride, 3 : 4 : 5 : 6-*tetrachloro*-2-p-*anisoylbenzoic acid*, m. p. 182°, and some of the dimethyl ether of phenoltetrachlorophthalein (compare Orndorff and Black, A., 1909, i, 389) are formed. The acid gives a *sodium salt*, $C_{15}H_7O_4Cl_4Na,5H_2O$,

pearly leaflets, m. p. 275° (decomp.), a *potassium* salt,

$$C_{15}H_7O_4Cl_4K,4H_2O,$$

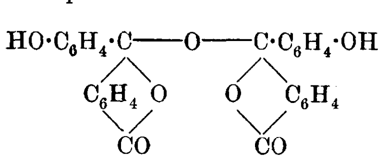
leaflets, the anhydrous salt having m. p. 245—248° (decomp.), and an *acetate*, $C_{17}H_{10}O_5Cl_4$, white needles, m. p. 225°. The acetate when heated with phenol at 180° for two hours yielded *phenoltetrachlorophthalein methyl ether*, white needles, m. p. 295° (decomp.).

The authors consider that the decomposition of phenolphthalein oxime is best explained by assigning to it the constitution (I), the oxime undergoing the Bechmann rearrangement to the compound (II) before decomposition. This is supported by the fact that

$$(C_6H_4\cdot OH)_2C{<}{N(OH) \atop C_6H_4}{>}CO \qquad OH\cdot C_6H_4\cdot C(OH){<}{N(C_6H_4\cdot OH) \atop C_6H_4}{>}CO.$$

(I.) (II.)

p-hydroxyphthalanil is obtained if excess of hydroxylamine is used in the preparation of the oxime. The hydroxyl groups in both 2-*p*-anisoylbenzoic acid and *p*-aminophenol, both being in the para-position, they must also occupy *para*-positions in phenolphthalein itself, which is therefore not a mixture of two isomerides. The easy and quantitative conversion of 2-*p*-anisoylbenzoic acid into phenolphthalein by heating the acid alone with phenol supports the theory that this acid is an intermediate product in the formation of phenolphthalein from phthalic anhydride and phenol.



The anhydride obtained from 2-*p*-anisoylbenzoic acid is assigned the annexed constitution. It resembles the phthaleins very closely in its properties and decomposes into phenolphthalein and phthalic anhydride when heated.

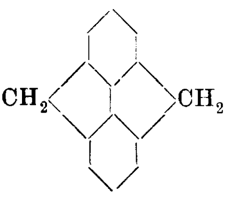
W. G.

Quinone-phenolate Theory of Indicators. Electrical Conductivity of Solutions of Phenolsulphonephthalein and of its Bromo- and Nitro-derivatives. E. C. White and S. F. Acree (*J. Amer. Chem. Soc.*, 1917, **39**, 648—652. Compare A., 1908, i, 653; 1909, i, 650).—The molecular conductivities and colours of approximately 0·001*N*-aqueous solutions of phenolsulphonephthalein, tetrabromophenolsulphonephthalein, and tetranitrophenolsulphonephthalein have been determined. The results show that these indicators are in the quinonoid form to the extent of at least 60%. The yellow colour is dependent on the quinone group and not appreciably on the primary ionisation, that of the sulphonic acid group. A comparison of the colours, conductivities, and p_H values of the first two of these substances with those of the last shows that the intense red or blue colours develop simultaneously with the secondary ionisation, that of the phenol group, and thus with the formation of quinone–phenolate ions.

J. F. S.

Some Products of the Reduction of 5-Nitro*iso*phthalic Acid. Richard Meyer and Hans Wesche (*Ber.*, 1917, **50**, 442—452).—In view of the possibility that a hydrocarbon of the

annexed formula might be present in coal tar or in the tar obtained during pyrogenic condensations of acetylene, the authors have tested various methods whereby it might be synthesised, but have found nothing serviceable yet.



Condensations between methylene chloride or carbonyl chloride and diphenyl or fluorene under the influence of aluminium chloride were entirely without result.

Another effort had for its aim the production of diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid, which ought to lose carbon dioxide on heating and give the diketone corresponding with the above formula. For this purpose, 5-nitro*iso*phthalic acid was treated as indicated, but the difficulties became too great at the stage of the benzidinetetracarboxylic acid :

$$NO_2\cdot C_6H_3(CO_2H)_2 \longrightarrow [(CO_2H)_2C_6H_3]_2N_2 \longrightarrow NH_2\cdot C_6H_2(CO_2H)_2\cdot C_6H_2(CO_2H)_2\cdot NH_2.$$

*iso*Phthalic acid is best nitrated by boiling with pure nitric acid. The alkaline reduction of 5-nitro*iso*phthalic acid may be effected by means of sodium amalgam or zinc dust, but best of all electrolytically. The product is *azobenzene*-3 : 5 : 3′ : 5′-*tetracarboxylic acid*, which crystallises in reddish-yellow filaments, decomp. 390°, and forms a *sodium* salt, $10H_2O$, bundles of yellow needles, and a *methyl* ester, reddish-yellow prisms, m. p. 223—224°. For the reduction and transformation of this acid, it is boiled with hydrochloric acid and tin, but much amino*iso*phthalic acid is always formed. *Benzidine*-2 : 6 : 2′ : 6′-*tetracarboxylic acid* crystallises in clusters of greenish-yellow needles, decomp. 300°.

The reduction of 5-nitro*iso*phthalic acid to an azoxy-acid is best effected by means of alkaline sodium arsenite solution. *Azoxybenzene*-3 : 5 : 3′ : 5′-*tetracarboxylic acid* crystallises in pale brown leaflets, decomp. above 360°, and the *methyl* ester in slender, pale yellow needles, m. p. 231—232°.

For the preparation of 5-amino*iso*phthalic acid, it is most convenient to reduce the nitro-acid with sodium hyposulphite. 5-*Acetylamino*iso*phthalic acid* crystallises in pale red needles, decomp. 314—315°, and the *benzoyl* derivative in prisms, decomp. above 360°. J. C. W.

Hemimellitic Acid. RICHARD MEYER and HANS WESCHE (*Ber.*, 1917, **50**, 452—455).—A further attempt to prepare diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid (preceding abstract) was by the electrolysis of a solution of *sodium* 1 : 3-*dimethyl hemimellitate*, $C_6H_3(CO_2Me)_2\cdot CO_2Na,6H_2O$, which crystallises in rectangular prisms, but this method also gave no result.

In methylating hemimellitic acid, the experience was gained that the fact that one of the carboxyl groups is surrounded by the others does not prevent its esterification, but only postpones it. J. C. W.

The Tinctorial Constituents of some Lichens which are used as Dyes in Ireland. HUGH RYAN and W. M. O'RIORDAN (*Proc. Roy. Irish Acad.*, 1917, **33**, 91—104).—A chemical examination has been made of four typical lichens which are used domestically for dyeing wool yellowish-brown shades, and a decision arrived at in each case as to the constituent to which the tinctorial properties are mainly due.

Parmelia saxatilis, Ach., yielded stereocaulic acid (soluble in ether) and salazinic acid (extracted by acetone), and although the latter is a colourless substance, it is the chief dyeing constituent, the dye proper being most probably an oxidation product.

Ramalina scopulorum, Ach., gave *d*-usnic and scopuloric acids, the tinctorial properties being due to the latter. It is suggested that salazinic and scopuloric acids are homologues of the formula $C_{17}H_{14}O_9$ and $C_{18}H_{16}O_9$ respectively.

Ramalina cuspidata, Nyl., yielded *d*-usnic acid, and the acid to which the dyeing properties are due was apparently cuspidatic acid, which might have the formula $C_{17}H_{16}O_{10}$.

Physcia parietina, De Not., is not used much for dyeing, and its chief constituent, physcione (frangula–emodin monomethyl ether), is practically devoid of tinctorial properties, which might scarcely be expected of a derivative of trihydroxyanthraquinone, if, as according to Fischer and Gross (A., 1911, i, 886), it is such a compound.

The chemical examination of these lichen acids agrees in the main with the classical work of Zopf and Hesse. J. C. W.

The *m*-Homosalicylaldehydes and their Derivatives. O. ANSELMINO (*Ber.*, 1917, **50**, 395).—The two aldehydes are obtained from *m*-cresol by the Tiemann-Reimer reaction and separated by conversion into their anils. 4-Methylsalicylaldehyde has m. p. 60—61°, and forms a solid anil, m. p. 93°, whilst 6-methylsalicylaldehyde has m. p. 32° and gives a liquid anil. The phenylhydrazones have m. p. 161° and 172°, and the semicarbazones 268° and 212—214° (decomp.) respectively (compare Chuit and Bolsing (A., 1906, i, 282). J. C. W.

A New Method for preparing Cyclic Ketones. FRITZ ULLMANN (*Ber.*, 1917, **50**, 403—405. Compare A. Schaarschmidt, this vol., i, 285).—Polemical. Questions of priority and patent specifications. J. C. W.

A New Synthesis of Aromatic Ketones. II. Artificial Production of Maclurin and Related Ketones. KURT HOESCH and THADÄUS VON ZARZECKI (*Ber.*, 1917, **50**, 462—468; 660. Compare A., 1915, i, 820).—An extension of Hoesch's process to more complicated phenolic ketones, culminating in the synthesis of maclurin.

Vanillonitrile (Marcus, A., 1892, 318) and phloroglucinol are dissolved in ether, mixed with anhydrous zinc chloride, and submitted

to a current of hydrogen chloride, when the ketone–imide hydrochloride separates as a crystalline mass. On boiling with water, this salt is hydrolysed to *vanillophloroglucinol* [*2:4:6:4′-tetrahydroxy-3′-methoxybenzophenone*], which crystallises in yellow needles, with $1H_2O$, decomp. above 200°. *Vanilloresorcinol* [*2:4:4′-trihydroxy-3′-methoxybenzophenone*] forms bundles of pale yellow needles, m. p. 210°.

Protocatechualdoxime, brilliant yellow needles, m. p. 157° (Wegscheider gave 149—151°, A., 1896, i, 612) is converted into *protocatechuonitrile diacetate* (*3:4-diacetoxybenzonitrile*), needles, m. p. 87°, by boiling with acetic anhydride, and this is hydrolysed to protocatechuonitrile, pale yellow needles, m. p. 156° (compare Ewins, T., 1905, **95**, 1488). This condenses with phloroglucinol in the above manner, forming maclurin (2:4:6:3′:5′-pentahydroxybenzophenone), the synthetic product being identical in properties with the natural substance. J. C. W.

Anisoylphenylethylene Oxide and other Keto-oxido-compounds. HENRIK JÖRLANDER (*Ber.*, 1917, **50**, 406—420. Compare this vol., i, 221—225).—The behaviour of anisoylphenylethylene oxide towards alkali hydroxides and acetic anhydride is described.

When boiled for a few moments with dilute alcoholic sodium hydroxide, the oxide suffers rearrangement into *anisyl ω-hydroxystyryl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot C(OH)\!:\!CHPh$, which crystallises in odourless leaflets, m. p. 98°, and gives a dark brownish-violet colour with ferric chloride. This compound is the enolic form of *anisylbenzylglyoxal* [*anisyl benzyl diketone*], $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot CH_2Ph$, into which it passes to a certain extent on keeping. This αα-diketone is conveniently obtained from the mono-oxime (below) by hydrolysis with hydrochloric acid. It is a yellow oil with an odour like that of benzaldehyde. It only reacts with ferric chloride after a time, and may be transformed into the enol by careful treatment with sodium ethoxide. Typical derivatives of the enol or diketone were obtained as follows: *benzoate*, leaflets, m. p. 117°; *3-anisyl-2-benzylquinoxaline*, needles, m. p. 137°; *anisyl benzyl diketonephenylosazone*, yellow prisms, m. p. 156°; *anisyl α-bromomenzyl diketone*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot CHBrPh$, pale yellow leaflets, m. p. 68°; *anisyl benzyl diketoxime*, leaflets, m. p. 194° (decomp.), by mixing the compound with hydroxylamine and sodium hydroxide in excess; *anisoylbenzylketoxime*, $OMe\cdot C_6H_4\cdot CO\cdot C(\!:\!N\cdot OH)\cdot CH_2Ph$, colourless needles, m. p. 109°, by boiling the compound with alcoholic hydroxylamine hydrochloride.

The constitution of this mono-oxime is proved by the fact that it can be obtained (in very small yield) by the action of amyl nitrite on *anisyl β-phenylethyl ketone*,

$$OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CH_2Ph,$$

colourless leaflets, m. p. 97°. This ketone is readily obtained by the reduction of anisoylphenylethylene oxide with zinc and acetic acid or less economically from benzylidene-*p*-methoxyacetophenone. In the latter reduction, *γδ-diphenyl-αζ-dianisylhexane-αζ-dione* is

also formed as a mass insoluble in alcohol, but crystallising from nitrobenzene in colourless needles, m. p. 251°.

If the original oxide is boiled with sodium hydroxide for a longer period, the diketone first formed suffers the benzil transformation into *α-hydroxy-β-phenyl-α-anisylpropionic acid*, prisms, m. p. 182° (decomp.), and a smaller quantity of another acid which is more soluble in alcohol and may be *α-hydroxy-β-phenyl-β-anisylpropionic acid*, prisms, m. p. 182° (m. p. of mixture, about 160°). When the former of these acids is boiled with acetic anhydride and sodium acetate, it loses the elements of water and forms *β-phenyl-α-anisylacrylic acid*, needles, m. p. 132—133°. This gives a dark red solution in sulphuric acid, and on diluting and adding alkali hydroxide the colour changes to dark bluish-violet. If boiled for a few moments with acetic anhydride and sulphuric acid, however, the above hydroxy-acid yields *3-acetyl-2-anisylindone*,

$$C_6H_4<\begin{matrix}CAc\\ -CO\end{matrix}>C\cdot C_6H_4\cdot OMe,$$

pale red, microscopic needles, m. p. 241°, whilst glacial acetic acid and sulphuric acid convert it into *2-anisylindone*, a dark red powder, m. p. 263—265°.

Anisoylphenylethylene oxide does not react with acetic anhydride alone, even on boiling, but if the agent is mixed with sulphuric acid, a certain amount of *anisoylphenylethylene glycol diacetate*, $OMe\cdot C_6H_4\cdot CO\cdot CH(OAc)\cdot CHPh\cdot OAc$, needles, m. p. 160°, is formed in the cold. This suffers rearrangement as well as hydrolysis when treated with sodium hydroxide or dilute sulphuric acid, the product being anisyl benzyl ketone, which crystallises in leaflets, m. p. 77° (Meisenheimer and Jochelson, A., 1907, i, 861), and may also be obtained by the oxidation of the above hydroxy-acid with potassium dichromate and acetic acid.

The above reaction whereby enolic forms of α-diketones can be prepared readily from ethylene oxides has been extended to other cases. Thus, benzoylphenylethylene oxide undergoes rearrangement into *phenyl ω-hydroxystyryl ketone*, $OH\cdot CBz\dot{:}CHPh$, which crystallises in many-sided forms, m. p. 85—86°, and yields a *benzoate*, rhombic leaflets, m. p. 108—109°, and 2-phenyl-3-benzylquinoxaline (Widman, A., 1916, i, 407). The compound separates at first as a yellow oil, which contains the ketonic form, phenyl benzyl diketone. As in the above case, this α-diketone may be obtained by hydrolysing the mono-oxime, benzoyl benzyl ketoxime (*iso*nitrosobenzylacetophenone), $CH_2Ph\cdot CBz\dot{:}N\cdot OH$ (Wieland, A., 1903, i, 836), which may be prepared from the enol. *Phenylbenzyldiketonephenylosazone*, m. p. 131°, *phenyl benzyl diketoxime*, m. p. 207°, and *phenyl α-bromobenzyl diketone*, m. p. 63°, are other typical derivatives obtained from the enol.

Benzoylphenylethylene oxide may also be converted, as in the above case of the anisoyl derivative, into *benzoylphenylethylene glycol diacetate*, $OAc\cdot CHBz\cdot CHPh\cdot OAc$, which crystallises in prisms, m. p. 107°, and may be transformed into deoxybenzoin by warming with alcoholic alkali hydroxide.

ω-Chloro-*o*-methoxyacetophenone (Tutin, T., 1910, **97**, 2503)

reacts with benzaldehyde to form o-*methoxybenzoylphenylethylene oxide*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH}<\begin{matrix}\mathrm{CHPh}\\ |\\ \mathrm{O}\end{matrix}$, which crystallises in colourless prisms, m. p. 124°, and may be transformed into o-*methoxyphenyl ω-hydroxystyryl ketone*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C(OH){:}CHPh}$, leaflets, m. p. 118°. 3-o-*Methoxyphenyl-2-benzylquinoxaline* is obtained from this in short prisms, m. p. 101·5°.

p-*Toluoylphenylethylene oxide*, leaflets, m. p. 85°, yields p-*tolyl ω-hydroxystyryl ketone*, prisms, m. p. 89—90°, and this, 3-p-*tolyl-2-benzylquinoxaline*, slender needles, m. p. 112—113°. It also forms p-*toluoylphenylethylene diacetate*, short prisms, m. p. 100°.

p-*Chlorobenzoylphenylethylene oxide*, needles, m. p. 123°, yields p-*chlorobenzoylphenylethylene diacetate*, short prisms, m. p. 110°, and also p-*chlorophenyl ω-hydroxystyryl ketone*, prisms, m. p. 103°, and this gives rise to 3-p-*chlorophenyl-2-benzylquinoxaline*, needles, m. p. 133°. J. C. W.

Unsaturated Ketones Derived from Diacetylorcinol. JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1917, **33**, 109—116).—Derivatives of diflavone and diflavanone having been obtained from benzylidene compounds of diacetylresorcinol (Ryan and O'Neill, A., 1915, i, 707, 1071), diacetylorcinol has been investigated for the same purpose. Several benzylidene derivatives are now described, but attempts to condense them to the desired compounds were not successful.

The product of the action of aluminium chloride at 160° on orcinol diacetate is identical with the diacetylorcinol described by Collie (T., 1904, **85**, 978). It forms a *dimethyl ether* (2:4-*diacetyl*-3:5-*dimethoxytoluene*), which is a colourless oil, b. p. 195—197°/30 mm., and it reacts with aldehydes in alcoholic-alkaline media to give benzylidene derivatives (distyryl diketones). The *dibenzylidene* compound, $\mathrm{C_6HMe(OH)_2(CO{\cdot}CH{:}CHPh)_2}$, is a pale yellow solid, m. p. 143—153°; the *dianisylidene* compound crystallises in orange prisms, m. p. 231—232°; the *diveratrylidene* compound forms orange-yellow prisms, m. p. 188—189·5°; the *dipiperonylidene* compound exists in one modification, "α," as orange-yellow prisms, m. p. 236—237°, and in a sparingly soluble form, "β," yellow prisms, m. p. 248—249°, which may possibly be a flavanone, for it seems to be produced from the α-form by the action of hot hydrochloric acid. J. C. W.

Reduction in Concentrated Sulphuric Acid Solution by Means of Aluminium Powder. ALFRED ECKERT and RUDOLF POLLAK (*Monatsh.*, 1917, **38**, 11—17).—The authors have studied the reaction described in D.R.-P. 190656 and 201542, by which anthraquinone derivatives are reduced in concentrated sulphuric acid solution by either copper or aluminium powder. In order to carry out the reduction, they dissolve the substance in 20—30 times its weight of concentrated sulphuric acid, and to the well-cooled mixture one-fifth of the weight of substance of aluminium powder

is slowly added with continuous shaking and cooling. The end of the reaction is indicated by foaming. When the reduction is complete, the mixture is poured into cold water and the product extracted with a suitable solvent. In this way, anthraquinone has been reduced to anthraquinol and anthrone; benzophenone into β-benzpinacolin; benzoylbenzoic acid into the dilactone of dihydroxytetraphenylethanedicarboxylic acid. If the reduction is effected with the further addition of acetic acid or benzoic acid or their anhydrides, the products are either the diacetylated or dibenzoylated derivatives of the reduced original substance. Thus, 5 grams of anthraquinone reduced by 1 gram of aluminium powder in 100 grams of concentrated sulphuric acid and 30 grams of glacial acetic acid yields the diacetyl derivative of anthraquinol. The dibenzoyl derivative is obtained in a similar manner. Acridone cannot be reduced by the above method. *p*-Chlorobenzoylbenzoic acid when reduced by aluminium powder yields the corresponding dilactone. When the dilactone of dihydroxytetraphenylethanedicarboxylic acid is heated with 20% fuming sulphuric acid for three hours at 180°, it is converted into sulpho-β-anthraquinonecarboxylic acid. J. F. S.

A Hydrate of Sodium Anthraquinone-2 : 7-disulphonate. M. L. Crossley (*J. Amer. Chem. Soc.*, 1917, **39**, 122—124).—The salmon-pink compound isolated in the separation of anthraquinone-2:6- and -2:7-disulphonic acids (compare A., 1915, i, 975) is shown to be a *hydrate* of sodium anthraquinone-2:7-disulphonate, the addition of the elements of water taking place, probably, through one of the carbonyl oxygens, this best accounting for all the properties of the substance. W. G.

The Caoutchouc from Eucommia ulmoides, Oliver. Arthur F. Sievers (*J. Amer. Chem. Soc.*, 1917, **39**, 725—731. Compare Weiss, *Trans. Linn. Soc.*, 1888—1894, [ii], **3**, 243).—An examination of the elastic constituent of *Eucommia ulmoides* with reference to its behaviour towards solvents. Qualitative and quantitative tests were made of its solubility in ether, light petroleum, toluene, chloroform, carbon disulphide, and carbon tetrachloride, and in this respect it was compared with samples of caoutchouc from Siam and Ceylon. The material from *Eucommia* does not swell up with the solvents, but becomes very soft and spreads over the bottom and sides of the containing vessel. W. G.

An Iodine Additive Product of Coumarin. Arthur W. Dox and W. G. Gaessler (*J. Amer. Chem. Soc.*, 1917, **39**, 114—117).—When an aqueous solution of potassium iodide (1 mol.) is added to an alcoholic solution of coumarin (2 mols.) and iodine (2 mols.), black, needle-shaped, lustrous crystals are formed, which seem to be an iodide of coumarin. When washed with

water, the compound decomposes into coumarin and iodine, and if treated with a solvent which does not dissolve potassium iodide, the only products obtained from the solution are coumarin and iodine. The compound contains from 30·5—31·7% of iodine, according to analyses, and a small, variable amount of potassium iodide, which probably is there as an impurity from the mother liquor. Substitution of the iodine in the coumarin molecule has not taken place, and the compound probably has the composition $(C_9H_6O_2)_4I_2$. W. G.

The Nitration Products of Tetrachlorofluoran and some of their Derivatives. W. R. Orndorff and J. J. Kennedy (*J. Amer. Chem. Soc.*, 1917, **39**, 88—103).—By nitrating tetrachlorofluoran under different conditions, five nitro-derivatives have been prepared, and subsequently reduced to the corresponding amino-compounds.

Tetrachlorofluoran is now found to have m. p. 290—291° (decomp.) (compare Orndorff and Black, A., 1909, i, 389). When nitrated in acetic acid solution with nitric acid (D 1·5), the mixture being heated to boiling, tetrachlorofluoran yields *tetrachloro-2-nitrofluoran*, m. p. 317—318°, which is practically insoluble in most of the ordinary organic solvents. It crystallises from glacial acetic acid. It dissolves unchanged in cold concentrated sulphuric acid. When reduced in an alcoholic solution of stannous chloride saturated with hydrogen chloride, it yields *tetrachloro-2-amino-fluoran*, m. p. 279—280°, which when diazotised and boiled with water gives tetrachlorofluoran instead of the expected hydroxyl derivative. If an excess of nitric acid is used in the above nitration, the product is a mixture of *tetrachloro-2:7-dinitrofluoran*, m. p. 317—318°, and *tetrachloro*iso*dinitrofluoran*, m. p. 249—250°, in which the nitro-groups are probably in the positions 2 and 5. These two isomerides are best separated by crystallisation from methyl alcohol, the first-named being the less soluble of the two. The 2:7-dinitro-compound when reduced as described above yields *tetrachloro-2:7-diaminofluoran*, orange needles, m. p. above 325°. The colour reactions correspond with those of diaminofluoran (compare Meyer and Friedland, A., 1898, i, 590). It gives a colourless *hydrochloride*. When diazotised in sulphuric acid solution and boiled with water, it yields *quinoltetrachlorophthalein*, faint yellow crystals, m. p. above 325°.

When tetrachlorofluoran is dissolved in nitric acid (D 1·5) and the solution heated on a water-bath, it yields *tetrachloro-2:5:7-trinitrofluoran*, yellow crystals, m. p. 275—276°; this on reduction gives *tetrachloro-2:5:7-triaminofluoran*, m. p. above 325°, which when diazotised and boiled with water gives a *phthalein*, which was not characterised.

Tetrachlorotetranitrofluoran, m. p. above 325°, was obtained by nitrating the trinitro-compound in a mixture of nitric acid (D 1·5) and sulphuric acid (D 1·84), or by nitrating the original tetrachlorofluoran in a similar mixture. On reduction it yielded *tetra-*

chlorotetra-aminofluoran, m. p. above 325°. No pentanitro-derivative could be obtained.

The nitro- and two isomeric dinitro-compounds are not affected by aqueous alkali hydroxides, but dissolve in hot alcoholic potassium hydroxide with a yellow colour. The tri- and tetra-nitro-compounds are slightly soluble in hot aqueous alkali hydroxides and readily so in cold alcoholic potassium hydroxide with an orange colour. In each case an ortho-quinonoid salt is probably formed. The salts of the tri- and tetra-nitro-compounds are quite stable, but the others are decomposed on the addition of water.

The amino- and diamino-tetrachlorofluorans dissolve in hot alcoholic potassium hydroxide with a yellow colour and the tri- and tetra-amino-compounds with a reddish-orange colour. The ortho-quinonoid salts probably formed are stable, no precipitation occurring on the addition of water.

The solubility of tetrachlorofluoran in concentrated sulphuric acid decreases with the successive introduction of nitro-groups into the molecule. W. G.

Condensation of Aldehydes with Ketones. III. Benzaldehyde with Methyl *iso*Propyl Ketone. Hugh Ryan and Phyllis Ryan (*Proc. Roy. Irish Acad.*, 1917, **33**, 105—108. Compare A., 1915, i, 416; 1916, i, 654).—In their explanation of the formation of a tetrahydropyrone, $C_{25}H_{22}O_2$, from benzaldehyde and dimethylacetylacetone or "monomethylacetylacetone," Ryan and Dunlea assumed that styryl ethyl ketone was an intermediate product. Later it was shown that this ketone did not give the same tetrahydropyrone when condensed with benzaldehyde, which rendered a revision of the explanation necessary.

It is now found that the compound in question is produced by the condensation of benzaldehyde with methyl *iso*propyl ketone, that is, with a hydrolytic product of dimethylacetylacetone, and not of monomethylacetylacetone. The wrong conclusion was mainly due to the fact that the monomethylacetylacetone used previously contained some of the dimethyl compound. The formula of the compound must therefore be altered to that of 2 : 6-*diphenyl*-3-*benzylidene*-5 : 5-*dimethyltetrahydropyrone*, and its formation be expressed by the scheme:

$$C_6H_5\cdot CHO + CHMe_2Ac \longrightarrow CHPh{:}CH\cdot CO\cdot CHMe_2 \xrightarrow{C_6H_5\cdot CHO}$$
$$O\Big<\begin{matrix}CHPh-CH_2\\ CHPh\cdot CMe_2\end{matrix}\Big>CO \xrightarrow{C_6H_5\cdot CHO} O\Big<\begin{matrix}CHPh\cdot C({:}CHPh)\\ CHPh\text{———}CMe_2\end{matrix}\Big>CO.$$

Pure methylacetylacetone condenses with benzaldehyde in alcoholic hydrogen chloride to form Ryan and Devine's compound, $C_{25}H_{20}O$, whilst ethyl α-acetylbutyrate gives *α-benzylideneacetylbutyric acid*, $CHPh{:}CH\cdot CO\cdot CHEt\cdot CO_2H$, m. p. 152° (decomp.). J. C. W.

Preparation of Cephaeline *iso*Amyl Ether and Salts Thereof. J. W. Meader (Brit. Pat., 103881, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 402—403. Compare this vol., i, 91).—*Cephaeline*

iso*amyl ether*, probably $C_{28}H_{37}O_3N_{20}\cdot C_5H_{11}$, is produced by treating cephaeline with an alkali metal and an *iso*amyl haloid. It is a varnish-like substance, easily soluble in alcohol, ether, or chloroform. It dissolves in acids to form salts, the *hydrobromide* crystallising in colourless needles. The ether and its salts are valuable medicinal products. H. W.

Chelerythrine. P. Karrer (*Ber.*, 1917, **50**, 212—221).—The most interesting facts known about the alkaloid chelerythrine (in plants of the order *Papaveraceae*) hitherto are that it is a colourless base which forms highly coloured salts and that it holds combined alcohol ($C_{21}H_{17}O_4N$,EtOH) and water ($\frac{1}{2}H_2O$) very firmly attached (compare Schmidt and co-workers, A., 1901, i, 742—744). It is now found to be a reactive substance. It contains a carbonyl group, and the remarkable discovery is made that any derivatives in which this group is altered, although they still contain nitrogen, are no longer basic. Chelerythrine, therefore, is the first alkaloid of which it can be said that it owes its basic properties to some atom other than nitrogen. It may be that an oxygen atom performs this function, the salts being oxonium salts.

Chelerythrine, recrystallised once from 96% alcohol, then four times from ethyl acetate, corresponds with the formula $C_{21}H_{17}O_4N$,EtOH, and has m. p. 199°. The hydrochloride, B,HCl,H_2O, crystallises well, and loses its water only after some days in an evacuated desiccator. From the salt, preparations free from alcohol, such as B,$\frac{1}{2}H_2O$, m. p. 250°, can be prepared by precipitation.

If to the orange-coloured solution of the hydrochloride is added a potassium cyanide solution, a *compound*, $(C_{21}H_{18}O_4N)\cdot CN$, is at once precipitated, which crystallises in colourless tablets or leaflets, m. p. 221° (another preparation gave 248°). This substance is indifferent to the action of dilute hydrochloric acid or sodium hydroxide, but the cyanogen residue is removed by boiling with alcoholic silver nitrate or concentrated hydrochloric acid.

The *phenylhydrazone*, $(C_{21}H_{19}O_4N)$:N·NHPh, m. p. 158°, is white, but gradually becomes brown even in a high vacuum. The *compound* with acetylacetone, $(C_{21}H_{19}O_4N)$:CAc$_2$, forms long, snowy needles, and the *compound* with *p*-nitrobenzyl cyanide, $(C_{21}H_{19}O_4N)$:C(CN)·$C_6H_4\cdot NO_2$, is pale yellow.

Grignard agents react with chelerythrine to give non-basic alkyl derivatives of a residue, $C_{16}H_{12}O_3N$, which is designated "*chelalbin*." *Methylchelalbin*, $C_{16}H_{12}O_3$NMe, *ethylchelalbin*, and *propylchelalbin* crystallise readily, but the m. p.'s depend on the m. p. of the original base.

Chelerythrine can also be reduced to the pure white, non-basic *dihydrochelerythrin*, m. p. 143—144°, by means of zinc or tin and hydrochloric acid. J. C. W.

The Alkaloids of the Pomegranate Tree. I. Pelletierine. Kurt Hess (*Ber.*, 1917, **50**, 368—379).—Of the five alkaloids which are recognised as constituents of the rind of the root of the

pomegranate tree (compare Tanret, A., 1878, 739; Ciamician and Silber, A., 1894, i, 154; and Piccinini, A., 1900, i, 110), only the crystalline ψ-pelletierine has been investigated at all closely and proved to be a homologue of tropinone. The main constituent, pelletierine, is an oil which is very sensitive towards atmospheric oxygen, and beyond the fact that it has the formula $C_8H_{15}ON$, little else is known about it. It is now demonstrated that it is a secondary base and that it contains a carbonyl group adjacent to a reactive methylene group. It cannot be a bicyclic base, but it may possibly contain a piperidine ring, although no evidence can be given as yet. These new facts are therefore summed up in the formula $C_6H_{12}(NH)(\cdot CO\cdot CH_2\cdot)$.

Pelletierine hydrochloride has m. p. 143—144°, and is not hygroscopic when pure, as Tanret stated; the *hydrobromide* crystallises extremely well in fan-like aggregates, m. p. 140°; the *picrate* has m. p. 150—151°. The N-*acetyl* compound, b. p. 173—174°/18 mm., and N-*benzoyl* derivative, prisms and plates, m. p. 75°, are formed by the action of the acyl chloride in the presence of sodium hydroxide. They are practically neutral, are stable, and yield *aurichlorides*, m. p. 95—96° and 139° (decomp.) respectively.

Pelletierine can be methylated by heating with formaldehyde and formic acid in a sealed tube at 135—143°. The *methylpelletierine* obtained in this way is an oil, b. p. 98—102°/14 mm., with a powerful narcotic odour, and is even more sensitive to air than pelletierine. The *hydrobromide*, $C_9H_{17}ON,HBr$, forms long, stable, prismatic needles, m. p. 152°, and the *semicarbazone hydrochloride*, prismatic rods, m. p. 168—169° (decomp.). Apparently, this base is not identical with Tanret's methylpelletierine or Piccinini's *iso*methylpelletierine, but these natural bases must be examined before a definite opinion can be expressed.

Pelletierine hydrobromide reacts with semicarbazide hydrochloride to give a double *compound* of the semicarbazone hydrobromide and semicarbazone hydrochloride, $C_{18}H_{38}O_2N_8ClBr,\frac{1}{2}H_2O$, m. p. 188° (decomp.). The simple *semicarbazone hydrochloride*, $C_9H_{19}ON_4Cl$, is obtained from the free alkaloid, in radiating groups of prisms, decomp. 188°.

The presence of one reactive methylene group, and the possibility of enolisation taking place, are shown by the formation of the following derivatives: iso*nitrosobenzoylpelletierine*, $C_{15}H_{18}O_3N_2$, long, thin tablets, m. p. 192—193°, by the action of amyl nitrite; *benzylidenepelletierine hydrochloride*, $C_{15}H_{20}ONCl$, m. p. 187°, and *benzylidenepelletierine chlorobromide*, $C_{30}H_{40}O_2N_2ClBr,H_2O$, m. p. 198°, by the action of benzaldehyde; *diacetylpelletierine*, $C_{12}H_{19}O_3N$, a very viscous, yellow oil, b. p. 145—155°/14 mm., which loses acetic acid when kept, but is stable towards oxygen and is formed by boiling pelletierine hydrobromide with acetic anhydride.

J. C. W.

Alkaloids of the Pomegranate Tree. II. Tanret's Methylpelletierine and Piccinini's *iso*Methylpelletierine. K. Hess and A. Eichel (*Ber.*, 1917, **50**, 380—384).—In order to investigate

these companion alkaloids of pelletierine, some root bark of the pomegranate has been treated according to Tanret and Piccinini's directions, when 40 grams of pure pelletierine hydrobromide and 21·5 grams of an oil containing the other bases were isolated from 100 kilos. of material. The oil has now been separated by fractionation under reduced pressure in an atmosphere of hydrogen into ψ-pelletierine, b. p. 140°/20 mm., m. p. 53—54° (Tanret gave m. p. 48°), and Piccinini's *iso*methylpelletierine, b. p. 100—115°/20 mm., picrate, m. p. 158°, semicarbazone hydrochloride, m. p. 208—209° (decomp.) (compare A., 1900, i, 110). No trace of Tanret's optically active methylpelletierine could be found in this specimen. Perhaps Piccinini's compound is the racemeride of Tanret's base, or more probably the latter was impure. The base is certainly not identical with, although so similar to, α-1-methylpiperidyl-2-propanone (A., 1916, i, 67). A very small quantity of a stable methylpelletierine quite identical with this ketone was found, however, in the first runnings, b. p. 101—103°/19 mm., of the above distillation. J. C. W.

Action of Aldehydes on Hydramines of the Pyrrolidine and Piperidine Series. IV. A Method for Alkylating Secondary Amino-alcohols. K. HESS, CL. UIBRIG, and A. EICHEL (*Ber.*, 1917, **50**, 344—351).—The alkylation of secondary amino-alcohols has always been difficult of achievement, even by the use of formaldehyde, because the hydroxyl group usually suffers oxidation in this process (A., 1916, i, 67). It has already been shown in one case, however (*ibid.*), that if formic acid is present, this substance undergoes oxidation more readily than the amino-alcohol, and so a *N*-methylated hydramine can be obtained. This is found to be a general reaction, and other examples are now given.

α-2-Pyrrolidylbutyl alcohol (*ibid.*) is heated with formic acid and 40% formaldehyde solution at 105—110° in a sealed tube, and so converted into α-1-*methyl*-2-*pyrrolidylbutyl alcohol*, a colourless oil with a faint, basic odour, b. p. 89—92°/16 mm., which forms a *picrate*, stout crystals, m. p. 113—114°, and an *acetate*, $\begin{matrix}CH_2-CH_2\\ |\qquad\quad \\ CH_2\cdot NMe\end{matrix}\!\!>CH\cdot CHPr\cdot OAc$, a limpid, mobile oil, b. p. 94—97°/13 mm., and resists the hydrolytic action of boiling hydrochloric acid.

β-6-Picolyl-2-ethyl alcohol is converted in like manner into β-1:6-*dimethylpyridyl*-2-*ethyl alcohol*, b. p. 114—118°/18 mm., which forms an *acetate*, b. p. 114—119°/16 mm.

The production of α-2-pyridylpropan-β-ol by the condensation of acetaldehyde with picoline is not economical. A yield of 54 grams from 940 grams of technical picoline is reported. This base, however, can be reduced quantitatively by means of catalysed hydrogen, and the specimen of α-2-piperidylpropan-β-ol obtained on this occasion had b. p. 114—115°/16 mm., crystallised in rectangular tablets, m. p. 69—70°, and yielded a *hydrochloride*, m. p. 133°. The methylation of this hydramine by the above process also proceeds smoothly. α-1-Methylpiperidyl-2-propan-β-ol (Ladenburg, A., 1898,

i, 688) is a pleasant-smelling base, b. p. 104—107°/10 mm., which forms a *picrate*, bundles of small rods, m. p. 178°, an *acetate*, b. p. 109—112°/17 mm., and a limpid, viscous *benzoate*, b. p. 176—178°/16 mm.

Scopoligenine can also be converted into very pure scopoline by methylation in this way. J. C. W.

Action of Aldehydes on Hydramines of the Pyrrolidine and Piperidine Series. V. Scission of Tertiary Methylamino-ketones into Formaldehyde and Secondary Hydramine Bases. K. HESS, A. EICHEL, and CL. UIBRIG (*Ber.*, 1917, **50**, 351—365. Compare A., 1916, i, 67).—In the case of some of the *tert.*-methylamino-ketones which were prepared by the action of formaldehyde on secondary hydramines, no direct proof of the presence in them of a carbonyl group could be obtained, for the usual reagents, hydroxylamine, semicarbazide, and phenylhydrazine, brought about the hydrolysis of the amino-ketone to the original hydramine and formaldehyde. It might conceivably be that in the case of 1-methyl-2-pyrrolidyl propyl ketone, for example, the compound is really an anhydride of the formula,

$$CH_2{<}\begin{matrix} CH_2\cdot CH\text{——}CHPr \\ CH_2\cdot N\cdot CH_2\cdot O \end{matrix} ,$$

and so, in order to decide definitely whether genuine *tert.*-methylamino-ketones can be hydrolysed in this way, α-1-methylpiperidyl-2-propan-β-one has been prepared by the oxidation of the corresponding *iso*propyl alcohol (preceding abstract) and tested in its behaviour towards semicarbazide. It is found that under one set of conditions the ketone yields a semicarbazone, whilst under others it is hydrolysed to α-2-piperidylpropan-β-ol and formaldehyde semicarbazone.

α-1-Methylpiperidyl-2-propan-β-ol is oxidised by means of chromic acid and acetic acid at 65—70°. α-1-*Methylpiperidyl-2-propan-β-one* is a stable, limpid oil, b. p. 107—112°/18 mm., with a pleasant, geranium-like odour. It dissolves in cold water in all proportions, but is precipitated almost completely on warming, and it reduces ammoniacal silver solutions, giving silver mirrors. The base acts locally as a powerful irritant. The *picrate* has m. p. 136—137°, and the *semicarbazone*, obtained by leaving the base with semicarbazide hydrochloride and potassium acetate in aqueous solution, crystallises in rhombohedra, m. p. 142—143°, and forms a *hydrochloride*, $C_{10}H_{20}ON_4,HCl,\frac{1}{2}EtOH$, m. p. 183° (decomp.). When the base is left with semicarbazide acetate in alcoholic solution, however, *formaldehyde semicarbazone*, $CH_2{:}N\cdot NH\cdot CO\cdot NH_2$, crystallises out gradually in stout prisms, m. p. 169° (decomp.), and α-2-piperidylpropan-β-ol (preceding abstract) may be recovered from the mother liquor.

The authors share the experience of Thiele and Bailey (A., 1899, i, 109) in being unable to obtain a normal semicarbazone by the direct application of formaldehyde.

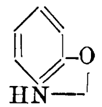
It was desired to effect the above hydrolysis with a specimen of 1-methyl-2-pyrrolidyl propyl ketone (A., 1916, i, 68), which should

be obtained by the oxidation of α-1-methyl-2-pyrrolidylbutyl alcohol (preceding abstract). It was found, however, that during the oxidation of this secondary alcohol the methyl group is also eliminated, the product being an imino-ketone which resembles pelletierine in properties.

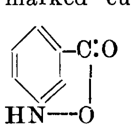
The Hofmann degradation has also been applied to 1-methyl-2-pyrrolidyl propyl ketone. When this ketone is treated with methyl iodide, it forms two quaternary *methiodides*; one is crystalline, m. p. 95°, and after treatment with silver chloride gives an *aurichloride*, $C_{10}H_{20}ONCl_4Au$, sulphur-yellow tablets, m. p. 93°, whilst the other is a syrup which similarly yields an isomeric, golden-brown *aurichloride*, m. p. 82°. When the corresponding ammonium hydroxides are distilled, they lose formaldehyde and yield the same *base*, $CH_2\colon CH\cdot CH_2\cdot CH(NHMe)\cdot CHPr\cdot OH$ or $NHMe\cdot CH_2\cdot CH_2\cdot CH\colon CH\cdot CHPr\cdot OH$, b. p. 89—91°/10 mm.

2-Pyrrolidyl propyl ketone, $\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2-NH \end{matrix}\!\!>\!CH\cdot COPr$, obtained by the oxidation of α-1-methyl-2-pyrrolidylbutyl alcohol by means of chromic acid, is a very strongly basic oil, b. p. 84—86°/17 mm., which very soon changes to a dark resin on exposure to the air. The *picrate* has m. p. 104—105°, the *picrolonate*, m. p. 128—129°, and the *semicarbazone* crystallises in rosettes of prismatic needles, m. p. 186° (decomp.). Although the authors do not doubt that the base is an imino-ketone, they have not been able to benzoylate it, and find that the methylation by means of formaldehyde and formic acid follows an abnormal course. The alkaline liquid left after extracting the base with ether was evaporated to dryness, when butyric acid was recognised in the vapour and hygric acid in the residue. J. C. W.

Chemical Nature of the "Vitamines." III. Structure of the Curative Modifications of the Hydroxypyridines. Robert R. Williams (*J. Biol. Chem.*, 1917, **29**, 495—520. Compare A., 1916, i, 697, 770, 862).—The author amplifies his previous directions for the preparation of the needle-crystal form of 2-hydroxypyridine. The corresponding crystal form of 3-hydroxypyridine, and the anhydrous forms of methylpyridone, trigonelline, and betaine also produce curative effects on polyneuritic birds. It follows that the curative form of 2-hydroxypyridine is a ψ-betaine which can be represented by the annexed formula.



On decomposing nicotinic acid hydriodide with silver oxide, the filtrate from the silver haloid, on being promptly injected into a polyneuritic bird, is found to possess marked curative properties. It is suggested that the nicotinic acid thus produced has a betaine structure (annexed formula), and that the curative properties of the vitamine fractions of yeast and rice polishings are due in part to the presence of this isomeric form of nicotinic acid or a polymeride or simple derivative of it. H. W. B.



Methylation of Cyclic Amino-acids. II. Synthesis of 1-Methylhexahydropicolinic and 1-Methylhexahydronicotinic Acids. K. HESS and F. LEIBBRANDT (*Ber.*, 1917, **50**, 385—389. Compare A., 1916, i, 75).—For the purposes of comparison with certain degradation products of pelletierine, the authors have methylated hexahydro-picolinic and -nicotinic acids by means of formaldehyde.

Nicotinic and picolinic acids are obtained by the oxidation of technical picoline by a process which is described in detail, and these acids are reduced by the Paal-Skita method.

Hexahydronicotinic acid (nipecotinic acid) forms a hydrochloride, m. p. 280° (decomp.), which is unstable in solution, especially at 70—80°. 1-*Methylnipecotinic acid* (1-*methylpiperidine*-3-*carboxylic acid*) is an unstable substance which has not been obtained crystalline, but is characterised by a *methyl* ester, b. p. 90—93°/15 mm. This is a strongly alkaline, limpid, highly refractive, viscous oil which provokes to sneezing, and forms an *aurichloride*, in bundles of stout, yellow prisms, m. p. 105°.

Hexahydropicolinic (pipecolinic) acid forms an *acetate*, m. p. 219° (decomp.), and *ethyl* 1-*methylpipecolinate* (1-*methylpiperidine*-2-*carboxylate*) is a limpid, refractive syrup, b. p. 92—96°/11 mm. J. C. W.

Anhydroximes. II. ROBERT EVSTAFIEFF ROSE and WINFIELD SCOTT, Jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 273—279. Compare A., 1911, i, 372).—*o*-Aldehydobenzoic anhydroxime when reduced by zinc in acetic acid gives phthalimidine, m. p. 150—151°, which is in part further reduced to dihydro*iso*indole. *o*-Acetylbenzoic anhydroxime under similar conditions gives 1-methylphthalimidine and 1-methyldihydro*iso*indole. 1-Methylphthalimidine when boiled with acetic anhydride and potassium acetate gives an *acetyl* derivative, colourless needles, m. p. 71°. β-Ketobutyric anhydroxime [3-methyl*iso*oxazolone] when reduced with zinc and acetic acid yields ammonia and butyric acid, there being no evidence of the formation of a tetratomic ring compound. W. G.

Nitration of Quinolone and Carbostyril Ethers. ADOLF KAUFMANN and VICTOR PETHEOU DE PETHERD (*Ber.*, 1917, **50**, 336—344).—The nitration of the lactam form of "carbostyril" (I), better known as quinolone, and of its *N*-alkyl derivatives, and of *O*-ethers of the lactim type (II), is described. It is shown that

$$C_6H_4{<}{\begin{matrix}CH{:}CH\\ NH.CO\end{matrix}} \qquad\qquad C_6H_4{<}{\begin{matrix}CH{:}CH\\ N{=}C{\cdot}OH\end{matrix}}$$

(I.) (II.)

the first nitro-group enters position 6 in each case, and that quinolone and 1-alkylquinolones ultimately yield 3:6:8-trinitro-derivatives, whereas the carbostyril ethers only give 6:8-dinitro-compounds.

Quinolone is most readily obtained by converting 1-methylquinolone into 2-chloroquinoline (Fischer, A., 1898, i, 383) and boiling this with dilute hydrochloric acid. When treated with cold con-

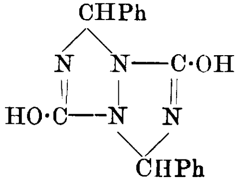
centrated nitric acid, this yields 6-nitroquinolone, m. p. 280° (the 6-nitrocarbostyril of Friedländer, A., 1885, 1139, and Cohn and Springer, A., 1903, i, 493). With a warm mixture of fuming nitric and sulphuric acids, however, the product is 3:6:8-*trinitroquinolone*, which crystallises in stellate groups of yellow needles, decomp. 176°, and forms *molecular compounds* with acenaphthene (red needles, decomp. 188°), α-naphthol (red spikes, detonating at 200°), and β-naphthol (red crystals, decomp. 206°). It is difficult to regulate the nitration so as to get a dinitro-compound, but 6:8-*dinitroquinolone*, white crystals, m. p. 218°, and the less soluble 3(?):6-*dinitroquinolone*, pale yellow needles, m. p. 253°, have been obtained in this way. The position of the 6- and 8-nitro-groups is determined by the fact that the above 3:6:8- and 6:8-compounds yield 3:5-dinitroanthranilic acid (leaflets, m. p. 268°) on oxidation with 1% permanganate.

1-Methylquinolone yields 3:6:8-*trinitro-1-methylquinolone*, m. p. 213° (compare Decker, A., 1901, i, 655). The positions of the nitro-groups are proved by the oxidation of the substance to 3:5-*dinitro-2-methylaminobenzoic acid*, delicate, yellow leaflets, m. p. 228—229°, which yields the known 3:5-dinitrosalicylic acid on warming with sodium carbonate.

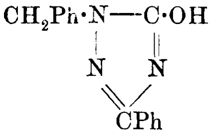
Carbostyril methyl ether is readily obtained by the action of sodium methoxide solution on 2-chloroquinoline. Unlike 1-methylquinolone, it forms a *picrate*, which crystallises in glistening, yellow needles, m. p. 170—171°. It yields 6-*nitro-2-methoxyquinoline*, white spikes, m. p. 189—190°, when mildly nitrated (obviously the nitromethylcarbostyril, m. p. 181°, described by Feer and Koenigs, A., 1885, 1235). The nitro-group affords some protection to the methyl group against hydrolysis, for the compound must be heated with hydrochloric acid under pressure in order to convert it into 6-nitroquinolone. 6:8-*Dinitro-2-methoxyquinoline* is obtained by warming the mono-derivative with nitrating mixture, in white needles, m. p. 206°, and this may be hydrolysed to the above 6:8-dinitroquinolone.

Carbostyril ethyl ether, b. p. 266°, 130°/12 mm., forms a *picrate*, $1H_2O$, yellow leaflets, m. p. 147°. 6-*Nitro-2-ethoxyquinoline* crystallises in white needles, m. p. 156—158°. J. C. W.

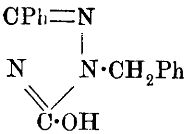
The Use of Cyanic Acid in Glacial Acetic Acid. II. The Addition of Cyanic Acid to Benzaldazine. J. R. BAILEY and N. H. MOORE (*J. Amer. Chem. Soc.*, 1917, **39**, 279—291. Compare A., 1915, i, 901).—Benzaldazine in glacial acetic acid readily takes up two molecules of cyanic acid, giving "5:3′-*dihydroxy*-3:5′-*diphenyldihydro*-1:2-*triazolotriazole*" (annexed formula), crystallising from alcohol in thin plates or prisms, softening at 207°, m. p. 234° (decomp.). This compound is soluble in alkali hydroxides, insoluble in cold hydrochloric acid. It is decomposed by cold concentrated sulphuric acid, giving off benzaldehyde. With formalde-



hyde it gives what is probably an additive product in the form of a gelatinous mass, which, however, gives up its formaldehyde again on drying. The "triazolotriazole" gives a *diacetyl* derivative, slender needles, m. p. 167° (decomp.). When dissolved in 10% aqueous potassium hydroxide and distilled with steam the "triazolotriazole" is decomposed, giving benzaldehyde, which distils over, and there is left in the flask benzaldsemicarbazone, which is insoluble in the alkali, and a *compound*, $C_{15}H_{13}ON_3$, short needles, m. p. 208°, which is precipitated on acidifying the solution with hydrochloric acid. This compound is considered to have the annexed constitution, and is isomeric with the triazole, m. p. 228° (see below).

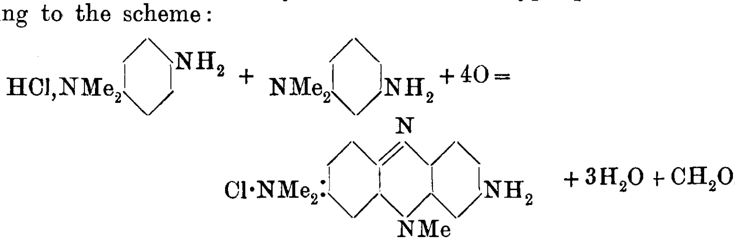


When the "triazolotriazole" is boiled with concentrated hydrochloric acid it slowly dissolves, being hydrolysed to benzaldehyde, hydrazine, and hydrazodicarbonamide. When oxidised with concentrated nitric acid at below 10° it gives 5-hydroxy-3-phenyl-1:2:4-triazole, m. p. 321—322° (decomp.) (compare Young and Witham, T., 1900, **77**, 226).



When benzylbenzylidenesemicarbazone is heated in a sealed tube with alcoholic ferric chloride for four hours at 125—135°, it is oxidised, giving 5-*hydroxy*-3-*phenyl*-1-*benzyl*-1:2:4-*triazole* (annexed formula), m. p. 228°, which is isomeric with the compound, m. p. 208°, described above. W. G.

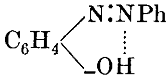
Tetramethyldiaminophenazine. P. KARRER (*Ber.*, 1917, **50**, 420—421). F. KEHRMANN and G. FALCONNIER (*ibid.*, 421—422).—The compound which Karrer obtained by oxidising a mixture of dimethyl-*m*- and dimethyl-*p*-phenylenediamines (A., 1916, i, 847) was not an azine but a dye of the safranine type, produced according to the scheme:



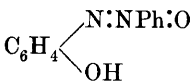
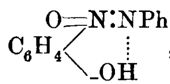
Karrer himself is led to doubt his earlier suggestion because true tetramethyldiaminophenazine has since been prepared by his colleague, Bauer, who will report on it. Kehrmann and Falconnier point out that Karrer's compound is insoluble in ether and contains a diazotisable amino-group. J. C. W.

Nitrosoarylhydroxylamines. VIII. Hydroxyazoxy-compounds and Nitrosophenylhydroxylamines. OSKAR BAUDISCH (*Ber.*, 1917, **50**, 333—336).—Most of the peculiarities of *o*-hydroxy-

azo-, -azoxy-, or -nitrosoarylhydroxylamino-compounds can be explained by formulæ which involve the phenolic hydroxyl group in union by residual affinities with one of the nitrogen atoms.

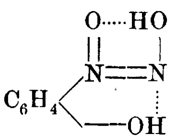
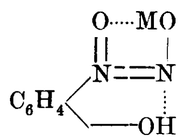
Thus, the formula  would explain why *o*-azophenol only combines with one molecule of ammonia and is not oxidised by silver oxide, whereas *p*-azophenol absorbs two molecules of ammonia and is readily oxidised to a quinoneazine, and *m*-azophenol is not oxidisable and combines with an intermediate amount of ammonia (Willstätter and Benz, A., 1906, i, 990).

The formula *A* for normal *o*-hydroxyazoxybenzene and *B* for the *iso*-compound (Bamberger, A., 1900, i, 531), explain the lack of

A.  and *B.*  ,

tinctorial properties, the resistance towards permanganate, and the insolubility in ammonia or sodium carbonate of the *iso*-compound, and also why 2 : 2′-dihydroxyazoxybenzene exists in only one form (following abstract).

Similarly, the formulæ *C* and *D* for nitroso-*o*-hydroxyphenylhydroxylamine and its salts, explain the influence of the position

C.  and *D.* 

of the hydroxyl group on the stability of these compounds (this vol., i, 331).

The importance of this internal salt formation between the azo- and *o*-hydroxy-groups is obviously of great interest in connexion with *o*-hydroxyazo-dyes. J. C. W.

2 : 2′-Dihydroxyazoxybenzene. Oskar Baudisch and J. Haftka (*Ber.*, 1917, **50**, 332).—This compound has been prepared for comparison with 2-hydroxyazoxybenzene (Bamberger, A., 1900, i, 531) and the 3 : 3′- and 4 : 4′-dihydroxyazoxybenzenes (A., 1904, i, 238; A., 1888, 1287).

o-Hydroxylaminophenyl *p*-toluenesulphonate (A., 1912, i, 442) is shaken with silver oxide in ethyl acetate mixed with anhydrous sodium sulphate, and then the green filtrate is boiled with a further portion of the ester until the dark brown liquid no longer reduces Fehling's solution. *2 : 2′-Di*-p-*toluenesulphonoxyazoxybenzene* is thus obtained, in straw-yellow crystals, m. p. 145—147°, and this yields *2 : 2′-dihydroxyazoxybenzene* on hydrolysis, in pale yellow, transparent rhombohedra, m. p. 154—155°. Unlike 2-hydroxyazoxybenzene, this compound exists in only one form, but, like it, it yields a brown copper salt. J. C. W.

Leucine Anhydride, a Product of the Hydrolysis of Protein by Water at High Temperatures. S. S. GRAVES and J. T. W. MARSHALL [with H. W. ECKWEILER] (*J. Amer. Chem. Soc.*, 1917, **39**, 112—114).—When casein is heated with water in an autoclave at 180—200° for sixteen hours and the product extracted with ether, a crystalline compound, m. p. 272°, is obtained and has been identified as leucine anhydride. Under similar conditions leucine itself only gives a trace of the anhydride, whilst leucylleucine gives more than a 90% yield of the anhydride. A number of proteins have been similarly treated, and the yields of leucine anhydride obtained were: casein, 1·5%; egg-albumin, 1·2%; edestin, 1·2%; Witte's peptone, 1·0%; silk, 0·09%; gelatin, 0·04%. W. G.

Auxo-amylases. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxxiv—xxxv; *J. Biol. Chem.*, 1917, **29**).—The accelerating influence of α-amino-acids on the hydrolysis of starch by ptyalin is not lost by substituting other radicles for the hydrogen of the amino-group. Thus, hippuric acid and glycine have a similar accelerating action on ptyalin. The substitution of a carboxyl radicle for the amino-group is attended with complete loss of activating power. Introduction of a sulphonic acid radicle also neutralises the effect produced by the amino-group; thus acid amides, including urea, and sulphanilic acid are devoid of accelerating power. The position of the amino-group, as in the isomeric aminobenzoic acids, does not modify the accelerating action on ptyalin. Compounds of amino-acids, like the proteins, also activate the enzyme.

As far as the author has investigated, pancreatic diastase and ptyalin are similarly affected by amino-acids. H. W. B.

Formation of Urea by Arginase and the Specificity of its Action. A. CLEMENTI (*Archiv di Fisiol., Florence*, 1916, **14**, 207—228; from *Physiol. Abstr.*, 1917, **1**, 508).—Hepatic arginase cannot resolve guanidylglycine into glycine and urea. Neither hepatic nor renal arginase splits creatine into sarcosine and urea. Arginase is also unable to split guanidylglycylglycine into glycylglycine and urea. G. B.

The Measurement of Oxidation Potential and its Significance in the Study of Oxydases. G. B. REED (*Bot. Gaz.*, 1916, **61**, 523—527).—In studying the rôle of plant oxydases, the author has tried with success a new method of following the progress of the oxidation reactions, namely, by measuring the oxidation potential of the solutions entering into the reactions. The apparatus consists essentially of a reaction cell in which is placed the solution to be tested with a platinum electrode dipping into the solution. The other half of the cell is a standard calomel electrode connected with the reaction cell by a syphon. Measurement of the potential of the cell is made by the Poggendorf compensation method. L. M. U.

Preparation of Derivatives of Arsenobenzene containing Nitrogen. FARBW. VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 294276; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—3:5-Dinitro-4-dialkylaminobenzene-1-arsinic acids are treated with reducing agents. The preparation of *tetramethylhexaminoarsenobenzene*, *tetraethylhexaminoarsenobenzene*, and *dipiperidinotetraminoarsenobenzene hydrochlorides* is described. The products have a higher therapeutic value and a more pronounced action on certain parasites than the corresponding dialkyl compounds. H. W.

Preparation of Thiocarbamide Compounds of Arsanilic Acid, its Homologues and Derivatives. H. THOMS (D.R.-P., 294632; from *J. Soc. Chem. Ind.*, 1917, **36**, 403).—Arsanilic acid or a homologue or derivative is treated with allylthiocarbimide, using methyl alcohol as solvent. The products have the combined therapeutic action of allyl and arsenic compounds, without exhibiting the poisonous character of the latter. The *compound* of allylthiocarbimide and arsanilic acid has m. p. 185° (decomp.), and is almost insoluble in water and alcohol, sparingly soluble in methyl alcohol. The corresponding *compound* of methylarsanilic acid darkens and intumesces at 170° without melting. H. W.

Physiological Chemistry.

Micro-titration of Ammonia, with some Observations on Normal Human Blood. GEORGE D. BARNETT (*J. Biol. Chem.*, 1917, **29**, 459—462).—The author's procedure differs from the usual aeration–titration method in the employment of a micro-burette and 0·005*N*-alkali. By this method the amount of ammonia in fresh normal human blood is found to be about 0·03 mg. per 100 c.c., which increases rapidly on keeping and reaches 0·10 mg. within thirty minutes. H. W. B.

Nature of the Sugar in the Blood. HUGH MCGUIGAN (*Proc. Amer. Soc. Biol. Chem.*, 1916, xx–xxi; *J. Biol. Chem.*, 1917, **29**).—The author calls attention to the existence of a polysaccharide in the blood of the nature of dextrin, and suggests that estimations of the sugar in the blood should be made before and after hydrolysis in order that the ratio of the free to combined or complex sugar may be determined. H. W. B.

Carbohydrate Metabolism. XIV. Influence of Administration of Alkali on the Sugar Content of the Blood in Relation to the Acid-Base-producing Properties of the Diet. XV. Influence of Acid-forming and Base-forming Diets on the Sugar Content of the Blood. LOUISE MCDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 227—232, 233—243).—The authors find that in the normal rabbit the sugar

content of the blood is not significantly changed by variations in the acid-base content of the diet which are sufficient to cause a marked change in the hydrogen-ion concentration of the urine. The intravenous injection of dilute sodium carbonate solution into the rabbit does not usually lower the sugar content of the blood, although it sometimes has this effect (compare Underhill, A., 1916, i, 685). Any hypoglycæmia produced must apparently be due to some other cause than the mere increase in the alkalinity of the blood. H. W. B.

Partition of Non-protein Nitrogen in the Blood of Fresh-water Fish. D. WRIGHT WILSON and EDWARD F. ADOLPH (*J. Biol. Chem.*, 1917, **29**, 405—411).—The authors have estimated the total non-protein nitrogen, urea, ammonia, amino-nitrogen, creatinine, and creatine in the whole blood and in the plasma of several species of fresh-water fish, including ganoids and teleosts. The urea content of the bloods is unusually low, and the concentration in the plasma is less than that in the corpuscles. The major part of the total non-protein nitrogen of the blood consists of amino-nitrogen, and here also the corpuscles contain more than the plasma. The authors suggest that possibly in the fish nitrogen is excreted in the form of amino-acid instead of urea. Creatine occurs in unusually large proportions, especially in the plasma. H. W. B.

Amino-acid Nitrogen Content of the Blood of Various Species. JOSEPH C. BOCK (*J. Biol. Chem.*, 1917, **29**, 191—198. Compare this vol., ii, 159).—The amount of amino-acid nitrogen in the blood of various animals is constant for each species. The amino-acid nitrogen of bird's blood is about three times as high as that of a mammal. The corpuscles usually contain more amino-acids than the serum.

There is about 7 mg. of amino-acid nitrogen in 100 c.c. of normal human blood. Sex does not appear to influence this amount, but the figures for placental blood are distinctly higher. Considerable variations, ranging from 4·5 mg. to 30 mg. per 100 c.c. of blood, occur in pathological conditions, higher figures being observed particularly in nephritis and uræmia. H. W. B.

Creatine and Creatinine in Whole Blood and Plasma. D. WRIGHT WILSON and E. D. PLASS (*J. Biol. Chem.*, 1917, **29**, 413—423).—The authors describe a modification of Folin's method for estimating the preformed creatinine and total creatinine (creatinine + creatine) in the whole blood, in which the blood proteins are removed by heating in dilute acetic acid solution, followed by treatment with aluminium hydroxide. Folin's method is regarded as satisfactory when applied to serum or plasma, but not when used for the whole blood.

By their method, the authors find from 2 to 5·2 mg. of total creatinine per 100 c.c. in the whole blood of various animals, which were presumably normal. Human blood contains about 3 mg. per 100 c.c. These figures are much lower than practically all data given by other workers (compare Folin and Denis, A., 1914, i, 764). Larger amounts of creatine are found in the plasma of infants than

in that of adults. The blood plasmas of the pig and of the hen contain even larger quantities. Corresponding with these high figures, there is a greater excretion of creatine in the urine. A characteristic relationship appears to exist between the concentration of creatine in the plasma and the amount eliminated in the urine.

H. W. B.

Fibrin Excretion under the Influence of an Electric Current. E. HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 900—903).—The clotting of blood consists in the formation of a fibrin gel, which is insoluble in water, but may be transformed into a sol by the action of very dilute solutions of acid or alkali hydroxide. By neutralising the acid or alkali sols the fibrin separates out again in gel form. The same result is obtained when an electric current is passed through the sols. Coagulation occurs at the positive electrode with alkali sols and at the negative with acid sols. The fact that natural fibrin sols also show gel formation at the positive electrode under the influence of a current is considered to show that in the clotting of blood the fibrin is converted from the alkali sol into the gel condition. H. M. D.

The Digestibility of Bread. II. Salivary Digestion of Erythrodextrin in Vitro. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1917, **39**, 315—320. Compare A., 1916, i, 578).—The digestion of erythrodextrin by ptyalin is a unimolecular reaction, the optimum temperature for which is 51°. At the ordinary temperature the temperature-coefficient is relatively small. At 65° the enzyme is killed. When the ratio of substrate to enzyme is very large, the digestion becomes disproportionately slow, this ratio being constant for different concentrations. It is suggested that it represents a union of enzyme and the substrate prior to hydrolysis. Maltose only exerts a relatively small retarding influence on this digestion, the influence varying directly with the concentration of the maltose.

W. G.

The Assumed Destruction of Trypsin by Pepsin and Acid. II. Observations on Animals. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1917, **39**, 162—174. Compare A., 1916, i, 770).—Experiments were carried out on dogs to determine the combined effect of pepsin and hydrochloric acid on trypsin, under conditions which correspond with those obtaining in the human stomach at times, when the latter ferment is ingested. The trypsin was fed either with or without meat and the stomach contents were secured by one of four methods, namely, (*a*) by means of a tube after the ligation of the pylorus, the organ thus constituting a closed pouch in which the secretion followed normally for a time; (*b*) from the normal, open stomach by the tube applied at the proper interval after the ingestion of food and trypsin; (*c*) by means of a gastric fistula made in the normal organ and opened from time to time for the withdrawal of the contents; (*d*) from a false stomach or Pavlov pouch constructed from the normal organ.

In all cases the secretion of pepsin and acid was abundant, and thus the conditions for the persistence of trypsin were not favourable. In the larger number of experiments, however, the trypsin was not destroyed by the pepsin-acid combination where sufficient protein was present to reduce the acid concentration to a certain value. Only when the acid was in excess of the pepsin did the trypsin seem to be destroyed or greatly weakened. It is possible, therefore, that some tryptic digestion may occur in the human stomach when the free acid is very low from protein combination.

W. G.

Activation of Pancreatic Lipase by Cholates. (MLLE.) J. A. DE JONGE (*Arch. Néerland. Physiol.*, 1917, **1**, 182—197).—The extent of activation of pancreatic lipase by sodium cholate depends on the age of the pancreatic extract and appears to vary rhythmically as the age of the extract increases. A pancreatic extract, the activity of which is increased by the addition of sodium cholate, may at the end of a week have entirely lost the capacity for being thus activated. If this extract is kept for another week, it is found that the addition of cholate again begins to exert an activating action, and at the end of the second week the activation produced by the cholate may be greater than that observable with the original extract. At the end of the third week the activating capacity may have again vanished, and so on. A satisfactory explanation of this phenomenon, which was repeatedly observed, is not given by the author.

The addition of gum arabic to the pancreatic extract produces an activating effect owing to its emulsifying action on the substrate. This action is found to be independent of the age of the pancreatic extract. The specific action of sodium cholate is therefore different from that of gum arabic; it is not concerned with the emulsification of the substrate, but with a true activation of the enzyme, lipase (compare Donath, A., 1907, ii, 975). H. W. B.

Effect of Bile and Bile Salts on the Reaction between Oleic Acid and Sodium Hydrogen Carbonate. F. B. KINGSBURY (*J. Biol. Chem.*, 1917, **29**, 367—380).—The author describes experiments which demonstrate that the reaction between oleic acid and sodium hydrogen carbonate proceeds further in the presence than in the absence of bile, so that the presence of bile in the small intestine makes possible a much greater soap formation from the fatty acids liberated during digestion than could otherwise be the case with an alkali as weak as sodium hydrogen carbonate.

Attention is drawn to the erroneous statement in many text-books of physiological chemistry that the alkali of the small intestine, available for the neutralisation of the fatty acids, is sodium carbonate, instead of sodium hydrogen carbonate. H. W. B.

Vitamine Content of Brewers' Yeast. ATHERTON SEIDELL (*J. Biol. Chem.*, 1917, **29**, 145—154).—By feeding experiments it is shown that in the case of pigeons the vitamine deficiency of an

exclusive diet of polished rice is just replaced by daily doses of 0·5—1·0 c.c. of the clear filtrate from autolysed brewers' yeast. The deficiency is not replaced by doses of dried freshly pressed yeast approximately equivalent to 1 c.c. doses of autolysed yeast. Yeast which is autolysed before drying is more efficient than ordinary dried yeast.

On the assumption that the nitrogenous material removed by fullers' earth from the autolysed yeast filtrate consists of vitamine, it is calculated that a grown pigeon requires daily somewhat less than 1 mg. of vitamine. The diet, therefore, of a pigeon, and possibly also of man, must contain about 0·0033 per cent. of vitamine. H. W. B.

Maize as a Source of Protein and Ash for Growing Animals. ALBERT G. HOGAN (*J. Biol. Chem.*, 1917, **29**, 485—493).—Maize is deficient in calcium, tryptophan, and lysine. When these substances are added to the diet, the growth of rats is well maintained. H. W. B.

Dietary Deficiencies of the White Bean, Phaseolus vulgaris. E. V. McCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1917, **29**, 521—536).—The proteins of the white bean appear to have a low biological value. The carbohydrates in the bean are also particularly liable to undergo fermentation in the digestive tract, with the liberation of large quantities of gas. In some rats fed on the beans the distension of the intestinal tract with gas was apparently the direct cause of death. The beans are also deficient in the accessory substance, "fat soluble A," and in suitable inorganic constituents; but they are rich in "water soluble B," and may therefore be employed in small quantities to supplement food materials in which this accessory is missing or deficient. The addition of 25% of the beans to a diet containing adequate protein, salts, carbohydrates, and butter-fat (for fat soluble A) induces perfectly normal growth in rats with the production of normal litters of young, which in their turn make adequate growth on the same diet. H. W. B.

The Chemical Individuality of Tissue Elements and its Biological Significance. P. A. LEVENE (*J. Amer. Chem. Soc.*, 1917, **39**, 828—836).—An address delivered to a meeting of the Chemical Section of the A.A.A.S. in New York. W. G.

Ferments of Human Cerebro-spinal Fluid. ERICH LESCHKE and LUDWIG PINCUSSOHN (*Deut. med. Woch.*, 1917, **43**, 8—9).—Cavazzani's observations on the presence of glycolytic and amylolytic (diastatic) ferments were confirmed polarimetrically. In four cases of diabetes the glycolytic ferment was absent. The diastatic ferment is present in health and in various diseases, but only in small amount. Protective ferments (*Abwehrfermente*) never pass from the blood into the cerebro-spinal fluid, which circumstance the authors consider an important argument in favour of the origin

of the fluid as a specific secretion and against the view that it is of the nature of lymph or transudate. G. B.

Autolysis. V. Influence of Bile on Autolysis. H. C. BRADLEY and JOSEPH TAYLOR (*J. Biol. Chem.*, 1917, **29**, 281—288. Compare Tatum, A., 1916, i, 863).—The authors find that bile does not accelerate the autolysis of liver, spleen, kidney, thymus, or heart muscle. The rapid disintegration of cellular tissues when placed in bile observed by Tatum (*loc. cit.*) must therefore be due to cytolysis as distinct from autolysis. H. W. B.

Carbohydrate Metabolism. XVIII. Relation of Diet to the Glycogen Content of the Liver. LOUISE MCDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 255—263).—Although a large storage of glycogen in the liver of a rabbit may take place on an acid-producing diet, a still larger quantity is usually formed on a diet which yields a basic ash. The authors draw the conclusion that an excess of alkali favours the accumulation of glycogen. H. W. B.

Active Constituent of the Thyroid; its Isolation, Chemical Properties, and Physiological Action. E. C. KENDALL (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxix—xxx; *J. Biol. Chem.*, 1917, **29**).—Primary cleavage of the thyroid proteins yields acid-soluble and acid-insoluble compounds. The active iodine compound is included in the latter, and is isolated by taking advantage of the solubility of its barium compound in barium and sodium hydroxides. It is finally obtained in microscopic needles from alkaline alcohol by precipitation with acetic acid. The free base contains 65% of iodine, whilst the sulphate, which is soluble in alcohol, contains 60% of iodine and has a molecular weight of 586.

A dose of 0·125 to 0·25 mg. of the substance is sufficient in cases of cretinism, whilst amounts up to 2 mg. daily are tolerated in the human subject. Excessive doses administered to animals evoke symptoms of hyperthyroidism and eventually cause death. H. W. B.

Composition of Adipocere. R. F. RUTTAN and M. J. MARSHALL (*J. Biol. Chem.*, 1917, **29**, 319—327).—A specimen of adipocere from a pig has the following composition: Palmitic acid, 67·52%; other fatty acids, 24·34%; calcium soaps, 4·41%; fats and unsaponified matter, 2·24%; and protein, 0·665%. Besides palmitic, stearic, and oleic acids, two hydroxystearic acids were isolated and identified, namely, ι-hydroxy- and θ-hydroxy-stearic acids. These are characteristic of adipocere, and are probably derived from a portion of the oleic acid in the original fat by hydration. Neither margaric nor hydroxymargaric acids were detected; ammonium and other soluble soaps were also absent. It is evident that adipocere is the residue of the pre-existing fats of animals, and is composed almost entirely of the insoluble fatty acids left after the slow hydrolysis of the fats in the wet ground.

The protein matter has almost entirely disappeared, as well as the glycerol and soaps resulting from the hydrolysis of the fats.

The fatty acids, traces of fats, etc., soluble in ether constituted 94·1% of the adipocere, and gave the following constants: D^{100} 0·8436, n_D^{65} 1·436, and m. p. 60—63°. H. W. B.

Bioluminescence. II. Luciferin in Luminous Bacteria. III. Action of Oxydases. E. NEWTON HARVEY (*Amer. J. Physiol.*, 1916, **41**, 449—453, 454—463; from *Physiol. Abstr.*, 1916, **1**, 376).—II. R. Dubois's thermostable, oxidisable substance luciferin and his thermolabile enzyme-like substance luciferase, occur in the luminous organs of the mollusc *Pholas*, the beetle *Pyrophorus*, and in American fireflies. Impure luciferin can be prepared by precipitating luminous bacteria with alcohol, and will give light when mixed with firefly luciferase. The luciferase of bacteria is probably an endoenzyme, and has not yet been isolated from them. Oxydases for pyrogallol, guaiacum, etc., are also in an endoenzyme condition. Oxygen is necessary for light production; in the absence of oxygen, luciferase decomposes luciferin without the production of light. Firefly luciferase is readily destroyed by ether or chloroform, so differing from vegetable oxydases. Luciferin is not readily destroyed by these reagents. Luciferin of bacteria or firefly gives no light with potato-juice oxydase, with or without the addition of hydrogen peroxide.

III. Pyrogallol, even in very low concentration, gives off a yellow light about equal to that of luminous bacteria when oxidised by blood or plant oxydases in presence of hydrogen peroxide; the hydroxy- and amino-phenols do not act thus. Potassium ferricyanide, potassium permanganate, or ferric chloride may replace the oxydase. The light is brighter at 10° than at 0°. The light production is inhibited by potassium cyanide or by dilute acids and alkalis. Ether and chloroform have no effect. The oxydase is not a true catalyst, but transfers oxygen from the hydrogen peroxide to the pyrogallol. This mimics light production by luminous animals very closely. G. B.

Bioluminescence. IV. In Cypridina Hilgendorfii (Japanese Ostracod Crustacean); V. In Firefly; VI. In Cavernularia Haberi (Japanese Pennatulid). E. NEWTON HARVEY (*Amer. J. Physiol.*, 1917, **42**, 318—341, 342—348, 349—358; from *Physiol. Abstr.*, 1917, **2**, 4).—IV. The luminous secretion comes from the upper lip. It gives the luciferin–luciferase reaction. Luciferase is not an enzyme, as Dubois thinks, but is the source of light. The new name *photogenin* is proposed, and *photophlein* (light assister) is the new name given to luciferin. Oxygen is necessary. Both substances pass through a Chamberland filter and dialysing membranes; they are adsorbed by bone-black, and may be dried and extracted with ether without impairment. One part in 1700 millions of water gives visible light even at 0°. Photophlein occurs throughout the body, but photogenin in the luminous

organ only. The latter is the more stable, but is destroyed at 70°. Many other details are given.

V. The photogenin of the firefly is not so stable, and is destroyed at 42° and by fat solvents.

VI. Here the light arises from a slime secreted by the outer surface of the colony; the light is emitted by granules, which will pass through an alundum, but not a Chamberland filter, and do not dialyse; nor are they adsorbed by bone-black. The colony gives light on electrical stimulation. No light occurs in the absence of oxygen; the juice reduces methylene-blue and contains peroxydases and catalase. This animal does not give the photogenin–photophlein reaction but a faint light is obtained with a non-luminous *Cavernularia* juice (photogenin) and photophlein from *Cypridina* or firefly. G. B.

Preparation of Scyllitol from Dog-fish (Scyllium canicula). OTTO ROSENHEIM (*Proc. Physiol. Soc.*, vii—viii; *J. Physiol.*, 1917, **51**).—This optically active inositol, which is limited to Elasmobranch fishes, may be fairly readily prepared from the common dog-fish by extraction with acetone; yield, 1 gram from 10 kilos. G. B.

Adenine and Guanine in Cows' Milk. CARL VOEGTLIN and C. P. SHERWIN (*Proc. Amer. Soc. Biol. Chem.*, 1916, vi; *J. Biol. Chem.*, 1917, **29**).—The authors have isolated 500 mg. of adenine and 100 mg. of guanine from the protein-free residue from 100 litres of a mixed sample of cows' milk. These two bases have not hitherto been recognised in milk. H. W. B.

Acid-base Equilibrium in the Body. JOHN HOWLAND and W. McKIM MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1916, v—vi; *J. Biol. Chem.*, 1917, **29**).—The administration of hydrochloric acid in man leads to an increase in the titratable acid (A) and a proportionate increase in the ammonia (B) excreted in the urine, the ratio $A:B$ remaining constant. In the case of sodium dihydrogen phosphate, the titratable acid is increased, but the ammonia is unchanged, so that the ratio $A:B$ is greatly increased. Administration of phosphate mixtures of the same hydrogen ion concentration as that of normal blood is followed by a slight increase in the titratable acid and a distinct diminution in the excreted ammonia. These results are in accord with the clinical data, since, in cases of nephritis, which are accompanied by a retention of dihydrogen phosphate, the acidosis is attended with a low excretion of ammonia. In these cases, therefore, ammonia estimations do not give trustworthy information regarding the state of acidosis which may be existing. H. W. B.

Hourly Elimination of certain Urinary Constituents during Brief Fasts. ISAAC NEUWIRTH (*J. Biol. Chem.*, 1917, **29**, 477—484).—The amounts of uric acid, creatinine, and total nitrogen passed hourly in the urine of a young man during a

twenty-seven hours' fast vary considerably during the day. The last meal is taken at 6 p.m., and during the following morning there is a marked decline in the uric acid output, which becomes more gradual during the afternoon. A close correspondence occurs in the rise and fall of uric acid and total nitrogen. The creatinine output shows marked variations from hour to hour from unknown causes. It reaches a minimum towards the end of the afternoon.

H. W. B.

Diurnal Variations in Creatine Excretion. W. DENIS [with ANNA S. MINOT] (*J. Biol. Chem.*, 1917, **29**, 447—451).—The analyses of the urines of several patients suffering from various diseases show that whilst the day urines contain considerable quantities of creatine, the urines passed during the night are practically free from creatine. By collecting the urine more frequently, it is found that on a strictly creatine-free diet, the maximum excretion of creatine occurs about two hours after the most substantial meal of the day. This result indicates that creatine is of exogenous origin and that its excretion is directly dependent on the intake of food. H. W. B.

Rate of Excretion of Urea. III. Effect of Changes in the Concentration of Urea in the Blood on the Rate of Excretion of Urea. IV. Effect of Changes in the Volume of Urine on the Rate of Excretion of Urea. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1917, **29**, 391—398, 399—404. Compare A., 1916, i, 352, 864).—The rate of excretion of urea increases with increasing concentration of urea in the blood. A curve is constructed by the authors from data obtained from numerous persons showing the relation between these two factors.

After abstention from food and water, the drinking of large quantities of water is followed by an increase in the volume of urine and by a synchronous acceleration of the rate of excretion of urea, which cannot be accounted for on the basis of changes in the concentration of urea in the blood. The increased rate of excretion does not appear, however, to be the result of the increased volume of urine, since the degree of increase above the normal in the rate is quantitatively independent of the degree of increase in the volume. The authors conclude, therefore, that the rate of excretion of urea is not appreciably affected by changes in the volume or in the concentration of urea in the urine. H. W. B.

Experimental Glycosuria. XI. Retention of Dextrose. J. J. R. MACLEOD, M. E. FULK, J. H. DAVIS, and R. W. SCOTT (*Amer. J. Physiol.*, 1917, **42**, 193—213; from *Physiol. Abstr.*, 1917, **2**, 38).—Injection of large doses of dextrose into the portal and iliac veins and vena cava shows that in dogs the sugar-retaining power of the liver is about equal to that of the hind-limb muscles. Large amounts of dextrose raise the H-ion concentration of the blood; injection of sodium carbonate then lowers both the

H-ion concentration and the sugar content, but whether the liver or the muscles are responsible for this sugar retention is not clear.

G. B.

Carbohydrate Metabolism. XIX. Influence of the Intravenous Injection of Sodium Carbonate on the Hyperglycæmia and Glycosuria following the Subcutaneous Administration of Dextrose. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 265—272).—The results of these experiments on rabbits are so variable that the authors are unable to draw any definite conclusion. H. W. B.

Carbohydrate Metabolism. XX. Mechanism of Salt Glycosuria. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 273—280).—The results of previous work are confirmed (Underhill and Closson, A., 1906, ii, 243). The authors consider that the absence of concomitant hyperglycæmia justifies the conclusion that saline glycosuria is due to an increased permeability of the kidney (compare Hirsch, A., 1915, i, 744).

H. W. B.

Carbohydrate Metabolism. XVI. Relation of Adrenaline Glycosuria to Dosage and to the Character of the Diet. XVII. Influence of the Intravenous Injection of Sodium Carbonate on Adrenaline Hyperglycæmia and Glycosuria. LOUISE McDANELL and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1917, **29**, 245—250, 251—254).—Rabbits on a mixed diet excrete larger amounts of sugar after the administration of small amounts of adrenaline than when maintained on either an acid-producing diet or one yielding a basic ash. Intravenous injection of sodium carbonate reduces the influence of the minimum effective dose of adrenaline (0·3 mg. of adrenaline per kilo. of body-weight in the case of a normal rabbit), but it does not entirely prevent the occurrence of hyperglycæmia and glycosuria. Apparently, with the smaller dose of adrenaline, hyperglycæmia and glycosuria are diminished relatively less by sodium carbonate than when larger doses of adrenaline are employed (compare Underhill, A., 1916, i, 685). H. W. B.

Bence-Jones Proteinuria. II. A. E. TAYLOR, C. W. MILLER, and J. E. SWEET (*J. Biol. Chem.*, 1917, **29**, 425—435. Compare Taylor and Miller, A., 1916, i, 584).—Further experiments are described in which the effect of the injection of the Bence-Jones protein into the animal body has been ascertained. Normal dogs can utilise or catabolise moderate quantities of Bence-Jones protein injected intravenously or subcutaneously, but a limit is soon reached beyond which the protein is promptly excreted in an unchanged condition. In dogs suffering from moderate uranium poisoning this power of utilisation is absent, and the Bence-Jones protein is energetically hydrolysed and eliminated as proteose. Doses of uranium nitrate which provoke only moderate symptoms

rapidly become fatal when Bence-Jones protein is also injected into the circulation, probably on account of the toxicity of the proteose formed from the injected protein.

After the death of the patient whose urine furnished the material for the above experiments, the urine taken from the bladder contained 3·6% of Bence-Jones protein, besides considerable albumin; the pleural fluid contained 0·11% and the blood about 0·2% of Bence-Jones protein. It is clear, therefore, that the protein circulates freely throughout the body. H. W. B.

Animal Diastases. I. The Increased Diastatic Activity of the Blood in Diabetes and Nephritis. VICTOR C. MYERS and JOHN A. KILLIAN (*J. Biol. Chem.*, 1917, **29**, 179—189).—The diastatic power is measured by incubating 2 c.c. of the oxalated blood with 1 c.c. of a 1% solution of soluble starch and 7 c.c. of water in a centrifuge tube for exactly fifteen minutes at 40°. About 1 gram of dry picric acid is added and the liquid centrifugalised. The reducing power of 3 c.c. of the filtered supernatant fluid is then estimated by Myers and Bailey's method (A., 1916, i, 300).

The results indicate that in cases of nephritis there is a two- to three-fold increase in the diastatic activity of the blood, which may possibly be explained by a decreased excretion of diastase in the urine. In diabetes, a still more pronounced increase in the diastatic power of the blood is noted. The bearings of this established fact on the current views of the etiology of diabetes are indicated, but the authors are unable at present to offer a satisfactory explanation of the cause of the condition. H. W. B.

Effects of Intravenous Injection of Arginine on the Creatine Content of Rabbits' Muscle. W. H. THOMPSON (*Proc. Physiol. Soc.*, ii—iii; *J. Physiol.*, 1917, **51**).—Arginine carbonate injected into rabbits in doses of 2—3 grams was transformed into creatine to the extent of 14·5% of the possible. The greatest increase in the muscle creatine observed was 0·0450%, which is brought about in six hours (under urethane anæsthesia). G. B.

Chemistry of Vegetable Physiology and Agriculture.

Vital Stains. WERNER SCHULEMANN (*Ber.*, 1917, **50**, 402—403). SIEGFRIED SKRAUP (*ibid.*, 641—645. Compare A., 1916, i, 869).—Polemical. Mainly questions of priority. J. C. W.

Bacterial Decomposition of Polypeptides. ICHIRO OTSUKA (*Acta Scholae Med.*, Kyoto, 1916, **1**, 199—214; from *Physiol. Abstr.*, 1917, **2**, 15).—*Staphylococcus pyogenes aureus* and *Bacillus prodigiosus*, killed by toluene, resolve glycyl-*l*-tyrosine and glycyl-

tryptophan. Killed *B. coli*, on the other hand, which has no action on gelatin or blood serum, is also without effect on these dipeptides. The active cultures become inactive both as regards proteins and dipeptides, by filtration through a Chamberland filter. Comparison of proteolytic enzymes shows that trypsin remains active after filtration, but erepsin does not (compare Sasaki, this vol., i, 107). G. B.

Lactic Fermentation and Thallium Salts. Study on Heredity. CHARLES RICHET (*Ann. Inst. Pasteur*, 1917, **31**, 51—59).—Amounts of thallium nitrate less than 0·001 gram per litre do not exercise any influence on the lactic ferment, but when the concentration reaches 0·0125 gram per litre the fermentation is diminished by 10% and with 0·125 gram per litre by 50%. If, however, the ferment is first accustomed to thallium nitrate by being grown on a medium containing 0·75 gram per litre, then in the presence of thallium nitrate to the extent of 0·125 gram per litre it produces a higher acidity than if the salt is absent. This toleration is not established immediately, but may require a period of eight days, but once established the bacillus produces a higher acidity than does a normal bacillus in the presence of the same thallium nitrate concentration. This toleration, while taking an appreciable time to establish, proceeds by a system of brusque mutations. W. G.

The Formation of Starch by Moulds. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1917, **78**, 308—312).—Moulds (*Aspergillus* and *Penicillium*) when grown on sugar solutions (5—10%) in the presence of ammonium salts (1—5%) at temperatures varying from 30° to 37° produce a substance giving the reactions of starch in the mycelia and also in the culture fluid. These results were obtained when dextrose, lævulose, and sucrose were employed, but not with lactose or maltose. The conclusion was drawn that the starch is formed in the presence of free mineral or organic acids (derived from the ammonium salts) under the influence of an enzyme. S. B. S.

Rate of Turbidity in Beverages containing Maltose, Dextrose, or Maltose and Dextrose. A. W. HOMBERGER and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1917, **39**, 156—162).—Solutions containing either dextrose or maltose or equal weights of the two sugars and varying proportions of alcohol, carbon dioxide, and water were bottled under conditions which would prevent contamination from micro-organisms, and stored. Turbidity only occurred in those solutions which contained dextrose, the turbidity being due to the germination of the spores of *Penicillium glaucum*, the dextrose acting as a chemical stimulus. Maltose does not stimulate the spores of this mould, and hence maltose solutions do not grow turbid on keeping. The presence of alcohol and carbon dioxide has no appreciable effect on the appearance of the turbidity in dextrose solutions. W. G.

Direct Estimations of Permeability. R. P. WODEHOUSE (*J. Biol. Chem.*, 1917, **29**, 453—458).—The author estimates the permeability of certain marine cells by comparing the composition of the sap inside the cell with that of the sea-water outside. The cells employed are those of the marine alga *Valonia*, individual cells of which are so large as to yield from 1 to 5 c.c. of sap.

The cell sap contains sodium, calcium, only a trace of magnesium, and an abundance of potassium; whilst the sea water contains sodium, calcium, magnesium, and only a relatively small quantity of potassium. The sap also differs from sea water in being free from sulphate. During life, therefore, the semipermeable protoplasmic membrane possesses a selective permeability which renders it impermeable to sulphates and yet permits of an accumulation of potassium ions within the cell. This selective permeability is lost at death; dead cells invariably contain sulphates, and if living cells are killed and replaced in sea-water, sulphate can soon be shown to be present inside. H. W. B.

Exosmosis. S. C. BROOKS (*Amer. J. Botany*, 1916, **9**, 483—492).—The effect of salts on the permeability of the plasma membrane of cells was studied as follows. Strips of the peduncle of *Taraxacum officinale* Weber, were immersed in solutions of sodium chloride (0·22*M*), calcium chloride (0·16 or 0·17*M*), and cerium chloride (4·05*M*) for from fifteen to twenty minutes; they were then transferred to distilled water, and the rate of exosmosis was determined by the conductivity of the liquid. Sodium chloride increased the rate of exosmosis, calcium chloride decreased it, and cerium chloride first inhibited and then accelerated exosmosis. It was found possible to make up a balanced solution which left the permeability of the protoplasm unaltered. This consisted of 80 parts of sea-water to 20 parts of 0·52*M* calcium chloride solution, the whole diluted to 21/52 of the original concentration.

L. M. U.

A Study of Permeability by the Method of Tissue Tension. S. C. BROOKS (*Amer. J. Botany*, 1916, **10**, 562—570).—Strips of *Taraxacum officinale* Weber, when cut, curl outwards owing to the tension of the cells. If placed in slightly hypertonic solutions, their curvature first decreases and then increases until it exceeds the original curvature, indicating that the recovery of the plasmolysed cells has occurred. This phenomenon was taken as the basis of a method for determining the permeability of cells. The strips of tissue were placed in a slightly hypertonic solution, and the time of recovery was noted; then the concentration of the solution was gradually increased by the addition of measured amounts of a strong solution, and with each addition the time of recovery was observed again. Finally, the rate of penetration was expressed empirically by dividing the time of recovery by the increase in concentration of the solution. Assuming that the permeability remained normal in a balanced solution of sea-water and calcium chloride (see previous abstract), then salts of univalent cations

(sodium, potassium, ammonium) caused a rapid increase in permeability, whilst salts of bi- and ter-valent cations (calcium, magnesium, cerium, aluminium) caused a very great decrease in permeability. Sucrose penetrated the protoplasm quite rapidly and affected permeability like the univalent cations. L. M. U.

The Physiological Significance of Potassium in Plants. TH. WEEVERS (*Biochem. Zeitsch.*, 1917, **78**, 354—357).—According to the author, potassium salts play an important part in the formation of the proteins of plants. This conclusion is not in accordance with that arrived at by Stoklasa (A., 1916, i, 354). The results of this author are criticised, and it is claimed that his experiments were not carried out in the complete absence of potassium, and furthermore, that if his results as to the amount of protein are stated in absolute amounts instead of in percentages (on the dwarf plants produced when they are grown without potassium) the experiments do not indicate any production of protein. S. B. S.

Occurrence of Free Carbon Monoxide in Kelp (Nereocystis luetkeana). SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1917, **39**, 149—156. Compare Zeller and Neikirk, *Puget Sound Marine Stat. Pub.*, 1915, **1**, 25—30).—An examination of the gas contained in the floaters of the large Pacific coast kelp, *Nereocystis luetkeana*, does not confirm the results of Zeller and Neikirk (*loc. cit.*) as to the presence of appreciable quantities of carbon dioxide and the variation of the carbon dioxide and oxygen content with the time of day. The author now shows that the gas present in the floater contains carbon monoxide, the quantity varying considerably in different individual specimens over a range of from 0·2 to 12·4%, averaging 4%. The oxygen content was also higher than that found by Zeller and Neikirk, averaging 18%. The gas in the floater is under diminished pressure, the pressure readings being very irregular. At present there is no definite indication that the composition of the gas in the floater varies with the time of the day, that is, with the light intensity. The highest carbon monoxide content is to be found in the larger and more healthy kelps which grow where the tidal currents are swiftest. W. G.

Evidence of the Action of Oxydases within the Growing Plant. JOSEPH H. KASTLE and G. DAVIS BUCKNER (*J. Amer. Chem. Soc.*, 1917, **39**, 478—482).—A solution of phenolphthalin was injected into the centre of the stalk of sweet corn plants 6—7 ft. high at various distances below the tassel. The stalk was then cut off 8 in. below the point of injection, and cross-sections at once made at different intervals along the stalk. It was found on examination that the reagent had been completely oxidised to phenolphthalein. Similar results were obtained with a young stalk cut off just above the roots and the cut end inserted into a freshly prepared solution of phenolphthalin. Similar results were also

obtained with injection experiments with the okra plant. Oxidation must apparently, therefore, go on in the living cell. W. G.

Specific Action of Barium. W. J. V. OSTERHOUT (*Amer. J. Botany*, 1916, **9**, 481—482).—On placing certain species of *Spirogyra* in 0·0001*M*-barium chloride, a peculiar and very characteristic contraction of the chloroplasts was obtained. In the neighbourhood of the nucleus, the chloroplasts contracted so strongly that they formed a very compact, green mass like a twisted rope, the diameter of this mass being one-fourth to one-third of that of the cell. At the ends, little or no contraction occurred, and in no part of the cell did the protoplasm contract away from the cell wall, showing that this process is different from false plasmolysis, which may occur later if the exposure is sufficiently prolonged. Strontium chloride produced the same effect at higher concentrations (0·001*M* and higher), but the chlorides of calcium, magnesium, manganese, cadmium, nickel, cobalt, sodium, potassium, and ammonium did not at any concentration. L. M. U.

Copper in the Flora of a Copper-tailing Region. W. G. BATEMAN and LANSING S. WELLS (*J. Amer. Chem. Soc.*, 1917, **39**, 811—819).—An examination of the effects caused by the tailings of a large copper smelter on the native flora of the district. Most of the flora of the district seemed to have been destroyed, among the larger shrubs only the wild rose appearing to flourish. The plants grown in the region were found to contain appreciable amounts of copper, arsenic, antimony, and tin, the amounts of copper ranging from 0·0046% to 0·621%, being higher in the dead than in living tissues and greater in the bark than in other parts of the plant. W. G.

The White Turbidity of Wines. FONZES-DIACON (*Compt. rend.*, 1917, **164**, 199—200).—The examination of the precipitate formed in a white wine by atmospheric oxidation shows it to contain some organic matter in addition to mineral matter. The latter portion contains a very small amount of calcium, together with a larger amount of iron, which is combined with phosphoric acid in the proportion corresponding with basic ferric phosphate, $Fe_2O_3(P_2O_5)_2$. The precipitate is only obtained when the sulphurous acid, present in all white wines, is oxidised, and the presence of a trace of calcium, together with an excess of iron and phosphoric acid, are indispensable for its formation. The use of sulphurous acid solutions of ammonium phosphate in place of potassium metabisulphite in vinification appears to be one of the most important causes of this precipitation. W. G.

The Reactions of the White Turbidity of Wines. J. LABORDE (*Compt. rend.*, 1917, **164**, 441—443. Compare A., 1904, ii, 278).—A claim for priority over Fonzes-Diacon (preceding abstract). W. G.

The Turbidity of Wines. FONZES-DIACON (*Compt. rend.*, 1917, **164**, 650—652. Compare preceding abstracts).—The author admits the priority of Laborde, and points out that the modern process of vinification by sulphurous solutions of ammonium phosphate predisposes wines, and particularly white wines, to this turbidity ("casse"). It can be lessened or prevented by the addition of citric acid, but the legal amount is sometimes insufficient.

W. G.

The Phytic Acid of the Wheat Kernel and some of its Salts. P. W. BOUTWELL (*J. Amer. Chem. Soc.*, 1917, **39**, 491—503).—Phytin was extracted from wheat bran and the wheat embryo by a modification of the method used by Clark with Indian field mustard seed (compare T., 1914, **105**, 535). The phytin, so prepared, was free from inorganic phosphates and was shown to be a crystalline calcium–magnesium salt, insoluble in water. In composition it does not agree with any of the simple calcium–magnesium salts of inositol–hexaphosphoric acid. The carbon and phosphorus are present, however, as in phytic acid, in equal numbers of atoms. Free phytic acid was prepared from this phytin, and differed from the phytic acid previously described in that it was an amber-coloured solid, undergoing spontaneous decomposition while drying in a vacuum. Crystalline barium salts were obtained from the crude phytin, the salt crystallised from cold dilute hydrochloric acid having the composition $C_6H_{12}O_{24}P_6Ba_3,C_6H_{10}O_{24}P_6Ba_4,14H_2O$, and that crystallised from boiling dilute hydrochloric acid having the composition $2(C_6H_{12}O_{24}P_6Ba_3),C_6H_{10}O_{18}P_4Ba_3,15H_2O$. Phytin thus seems to exist in the wheat kernel as salts of inositol-phosphoric acid, phytic acid being an ester of inositol and phosphoric acid.

The second part of the paper deals with the activity of the phytase of wheat bran and embryo under different conditions (compare Anderson, A., 1915, i, 634). In 0·2% hydrochloric acid the activity of the phytase as indicated by the production of inorganic phosphoric acid is inhibited, being only about one-third of its activity in 0·1% hydrochloric acid, which is the optimum acidity. Dry heat increases the amount of inorganic phosphorus extracted from wheat-bran, without apparently destroying the enzyme. The activity of phytase is not affected by formaldehyde. W. G.

Assimilation of Organic Nitrogen by Zea mais and the Influence of Bacillus subtilis on such Assimilation. REED O. BRIGHAM (*Soil Sci.*, 1917, **3**, 155—195).—In the first part of the paper a historical survey of the work on this subject is given.

Two varieties of corn, namely, *Zea mais everta* (pop corn) and *Zea mais indentata* (dent corn), were grown on sterile 1% agar containing the necessary plant nutrients except nitrogen, this being added in the form of various organic substances and the effect on the plant growth observed either in the presence or absence of *B. subtilis*. The seeds were first sterilised, germinated on moist filter-paper in sterile petri dishes, and then the seedlings trans-

ferred to the agar. Units showing signs of infection were rejected.

Zea mais directly assimilates and uses the organic nitrogen supplied in the form of asparagine, casein, cotton-seed meal, hæmoglobin, linseed meal, uric acid, peptone, guanine, alanine, urea, creatine, malt, and glycine, named in the order of their availability. Guanidine carbonate and nitrate, diphenylamine, caffeine, and benzamide are toxic to *Zea mais*. Guanine is toxic to pop corn, but not to dent corn. Compounds containing a benzene nucleus were found to be exceedingly toxic to the plants tried. In the case of dent corn the six substances named first above were more effective than sodium nitrate in promoting growth, and ammonium sulphate is a far better source of nitrogen than sodium nitrate for this plant. The two varieties of *Zea mais* reacted differently with some of the nutrient substances.

In the presence of *B. subtilis* eight of the organic substances which were directly available produced better growth, probably because of ammonification. Generally speaking, those organic compounds of high complexity in composition are better after ammonification, whilst those of a low degree of complexity are not improved by ammonification.

The author considers that the method of determining growth by measuring the total length of the leaves gives results very nearly parallel to those obtained by determining the dry weights of the plant and is much simpler and quicker. W. G.

Non-specificity of the Animal and Vegetable Reducing Ferment. A. BACH (*Compt. rend.*, 1917, **164**, 248—249).—An examination of the reducing action of the ferment present in milk or potato pulp (compare A., 1916, i, 682) on nitrates in the presence of a number of aldehydes shows that it is independent of the complex to which the aldehyde group is attached. The specificity of the ferment is functional and not structural. Certain aldehydes are better utilised by the vegetable than by the animal ferment.

W. G.

Hydrolysis of the Soluble Protein of Swede Turnips. GWILYM WILLIAMS (*J. Agri. Sci.*, 1917, **8**, 182—215).—The author has prepared a quantity of the soluble protein from the expressed juice of swede turnips by precipitation, the juice being heated at 90° for half an hour. The protein thus prepared contained N = 14·09%; H_2O = 1·81%; ash, 8·60%; S = 4·204%. The value for the sulphur is particularly high, much of it probably coming from the ash. The protein was hydrolysed and the amounts of the various amino-acids present determined, the following results being obtained, expressed as percentages of the dry ash-free protein: Glycine, 0·27%; alanine, 3·58%; valine, 9·95%; leucine and *iso*leucine, 9·01%; phenylalanine, 4·47%; tyrosine, 2·92%; cystine present; proline, 4·17%; aspartic acid, 6·98%; glutamic acid, 3·18%; tryptophan present; arginine, 3·12%; histidine, 3·04%; lysine, 4·35%; ammonia, 1·21%; humin substances, 4·74%; total, 60·99%. The protein shows no excessive content of any particular amino-acid

and all the usual "Bausteine" are present. The glutamic acid content is low as compared with other vegetable proteins and the valine content unusually high. W. G.

The Organic Matter of the Soil. IV. Some Data on Humus-phosphoric Acid. ROSS AIKEN GORTNER and WILLIAM M. SHAW (*Soil Sci.*, 1917, **3**, 99—111. Compare this vol., i, 248, 310, 311).—Estimations have been made of the phosphoric acid content of the ammonia extracts of eight soil types, peats, and unchanged vegetable materials, before and after leaching with 1% hydrochloric acid, and also of the amount extracted by this acid. Four per cent. ammonium hydroxide extracted more phosphoric acid from the air-dry soil in seven of the eight soil types than did the 1% hydrochloric acid. There is no apparent relation between the amounts of phosphoric acid extracted by the ammonium hydroxide before and after the soil was leached with 1% hydrochloric acid. The greater part of the phosphoric acid present in humus ash is probably inorganic, being derived from collöidal clay and from adsorption by the colloids present. There is no apparent relationship between the total nitrogen in the soil and the phosphoric acid extracted by the different treatments. The phosphoric acid present in the ammonia extract of soils cannot be correlated either with the organic matter present or with the known fertility of the soil type. The humification of vegetable materials in contact with a soil for a year did not increase the humus-phosphoric acid over that contained in the original subsoil. W. G.

α-Crotonic Acid, a Constituent of the Soil. E. H. WALTERS and LOUIS E. WISE (*Journ. of Agric. Res.*, 1916, **6**, 1043—1045; from *Chem. Zentr.*, 1916, i, 121—122).—The authors have isolated α-crotonic acid, m. p. 72°, from a barren, fine sandy loam from Texas, which formed a layer eight to eighteen inches thick over impervious clay. The soil was poor in lime and other bases, very faintly dehydrated, and had a high reducing and only very low oxidising action. For the isolation of the acid, the soil was treated for twenty-four hours with sodium hydroxide solution (2%) at the ordinary temperature; the extract was faintly acidified with sulphuric acid and extracted with ether. The ethereal solution was shaken with sodium hydrogen sulphite to remove aldehydes and other substances, and the sulphite solution repeatedly agitated with fresh ether. α-Crotonic acid was isolated from the brown, syrupy residue obtained by evaporating the ethereal extracts, 94 mg. of acid being obtained from 22·5 kilos. of soil. Owing to experimental losses, this figure must be regarded as a minimum value. The acid may possibly be formed from the β-hydroxy-acids obtained by the decomposition of cellulose or from allyl cyanide which is present in the ethereal oils of certain plants. H. W.

Organic Chemistry.

The Aliphatic Terpenes. C. J. Enklaar (*Rec. trav. chim.*, 1917, **36**, 363—365. Compare this vol., i, 111).—Polemical. A reply to Auwers and Eisenlohr (compare A., 1911, ii, 782).

W. G.

Preparation of Nitromethane and Homologues. H. Krause (D.R.-P., 294755; from *J. Soc. Chem. Ind.*, 1917, **36**, 520). —An intimate mixture of a nitrite and a salt of an alkyl hydrogen sulphate is made into a cream with water and distilled. Above 100° the nitroparaffin passes over, and this continues after the mass has been evaporated to dryness. Decomposition of the alkyl sulphate to form sulphuric acid or an acid sulphate is to be avoided, since it causes a loss of yield which is further augmented because the free sulphuric acid liberates nitrous acid, which then reacts with the nitroparaffin. To obviate this, a little alkali, or a salt with an alkaline reaction, is added to the mixture previous to distillation. The yield of nitromethane is 50%, of nitroethane 35%, of that theoretically possible.

H. W.

Preparation of Glycols. Gulf Refining Co. (U.S. Pat., 1215903; from *J. Soc. Chem. Ind.*, 1917, **36**, 472).—Glycols are obtained by heating dichloro-olefines under pressure with an alkali formate and an alcohol, for example, methyl alcohol. The temperature may vary between 140° and 200° and the pressure from 7 to 18 kilos. per sq. cm.

H. W.

Preparation of Acetic Acid from Acetaldehyde. Badische Anilin- & Soda-Fabrik (D.R.-P., 294724; from *J. Soc. Chem. Ind.*, 1917, **36**, 503).—Acetaldehyde is oxidised by air or oxygen in presence of iron compounds and organic salts of alkalis or alkaline earths, including magnesium and aluminium. The reaction is accelerated without the formation of per-acids. It proceeds rapidly and completely in the cold.

H. W.

Hydrogenisation and Dehydrogenisation of Carbon Compounds. Badische Anilin- & Soda-Fabrik. (U.S. Pats. (*A*), 1215334, (*B*) 1215335; from *J. Soc. Chem. Ind.*, 1917, **36**, 473. Compare A., 1915, i, 765).—Specific claim is made for the use, as catalysts, of mixtures of (*A*) nickel and boron oxide, and (*B*) nickel and calcium phosphate.

H. W.

Complex Organic Manganese Compounds. II. P. E. Verkade (*Chem. Weekblad*, 1917, **14**, 420—425. Compare *ibid.*, 34).—α-Hydroxy-acids, as well as pyruvic acid, malonic acid, and certain of their alkyl derivatives, react with hydrated manganese dioxide to form brown solutions, which are rapidly decomposed by heat, with formation of carbon dioxide, an aldehyde or ketone with

one carbon atom less than the parent acid, and the manganese salt of the acid. Aromatic hydroxy-acids form similar coloured solutions, but these are not decomposed by heat. A. J. W.

A Compound of Ethyl Oxalate with Potassium Tri-iodide. A. SKRABAL (*Ber.*, 1917, **50**, 581—582).—When a fresh solution of ethyl oxalate is mixed with iodine dissolved in potassium iodide, large, lustrous, polychroic (golden to dark blue) crystals are gradually deposited. The *compound* is apparently an oxonium periodide of the formula:

$$CO_2Et\cdot CO\cdot\underset{K}{\overset{Et}{O}}\text{——}\underset{I{:}I_2}{\overset{Et}{O}}\text{—}CO\cdot CO_2Et\ .$$

J. C. W.

The Formation and Decomposition of some Organic Halogenated Compounds. EINAR BIILMANN (*Rec. trav. chim.*, 1917, **36**, 313—328).—A quantitative study of the action of bromine water on certain unsaturated acids. The acids examined were fumaric, maleic, mesaconic, itaconic, acrylic, and crotonic acids. The results show that the bromine enters these acids principally in the form of hypobromous acid, $CO_2H\cdot CH{:}CH\cdot CO_2H + Br_2 + H_2O = CO_2H\cdot CHBr\cdot CH(OH)\cdot CO_2H + HBr$. In the case of fumaric and crotonic acids this is almost the total reaction, but with some of the other acids the reaction is partly of the type

$$CO_2H\cdot CH{:}CH\cdot CO_2H + Br_2 = CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H.$$

In the presence of a large excess of potassium bromide, there is a greater tendency for the second reaction to occur.

By measuring the initial velocities in solutions of very varied concentrations, the action of potassium iodide on $\alpha\beta$-dibromopropionic acid in the presence of sulphuric acid is shown to be bimolecular and to follow the course $CH_2Br\cdot CHBr\cdot CO_2H + 3KI = CH_2{:}CH\cdot CO_2H + 2KBr + KI_3$. The reaction is not reversible to any appreciable extent. W. G.

Rotatory Powers of Tartrates of Substituted Amines. LUIGI CASALE (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 434—438; *Gazzetta*, 1917, **47**, i, 191—196).—The author has measured the rotatory powers of a number of tartrates and hydrogen tartrates of the alkali metals and of a number of aromatic and aliphatic amines. From the numerical results obtained, the following conclusions are drawn.

In dilute aqueous solution and at the ordinary temperature the hydrogen tartrates of organic bases exhibit molecular rotations identical with those found for the hydrogen tartrates of the alkali metals, and are, therefore, not hydrolysed. Under the above conditions, the normal tartrates of aliphatic amines also possess molecular rotatory powers equal to those given by the corresponding alkali salts, and thus do not undergo hydrolytic dissociation. Under the same conditions, the normal tartrates of aromatic amines exhibit

molecular rotations which are markedly inferior to those shown by the corresponding salts of the aliphatic amines and increase with increase in the concentration of the base in solution; they are, therefore, partly hydrolysed.

These results disprove: (1) Kannonikov's statement, based on the equality of the specific rotations of normal tartrates of the weak bases to that of tartaric acid, that these tartrates undergo complete hydrolytic dissociation (A., 1892, 1308), and (2) Minguin and Wohlgemuth's conclusion that the acid salt formed by the combination of one molecule of tartaric acid with one molecule of an aromatic amine is very appreciably hydrolysed, and that the addition of further proportions of the base diminishes and finally annuls the hydrolysis (A., 1909, i, 11). T. H. P.

Pectin Substances. II. Algic and Fucic Acids. SVEN ODÉN (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 83—93. Compare this vol., i, 436).—The electrical conductivities of suspensions of algic and fucic acids (Kylin, A., 1915, i, 931) treated with dilute ammonium hydroxide undergo similar changes to those previously described (*loc. cit.*). Both substances are therefore true acids, forming soluble salts on treatment with alkalis. When gelatin is similarly tested, it is found to have very slight acidic properties, which may be due to impurities.

Fucic acid has the empirical formula $C_{10}H_{18}O_{11}$, mol. wt. 160, and properties which lead the author to suggest that the substance is a dipentonedicarboxylic acid, $O(C_4H_8O_3 \cdot CO_2H)_2$. H. W. B.

Crystallisation and Properties of a β-Monoglucoside of Glycerol previously obtained by Biochemical Synthesis. EM. BOURQUELOT, M. BRIDEL, and A. AUBRY (*Compt. rend.*, 1917, **164**, 831—833. Compare A., 1915, i, 703).—The glucoside prepared by the action of emulsin on a solution of glycerol and dextrose has now been obtained in a crystalline form from its alcohol–ether solution on long keeping. It crystallises in elongated prisms, m. p. 130—135°; $[\alpha]_D$ $-28°16'$, and does not reduce Fehling's solution. W. G.

Preparation of β-Ethyl Galactoside by means of the Kernels of Apricots, Peaches, and Cherries, the Seeds of Apples, and Bitter-almond Cake. MOUGNE (*J. Pharm. Chim.*, 1917, [vii], **15**, 345—348).—Using the β-galactosidase preparation obtained from the above sources (compare this vol., i, 438), the author has, in all cases, been able to synthesise β-ethyl galactoside from galactose and ethyl alcohol. W. G.

The Biochemical Synthesis of Alkyl Glucosides. IV. Alkyl Galactosides. EM. BOURQUELOT (*Ann. Chim.*, 1917, [ix], **7**, 153—226).—A résumé of work already published (compare A. 1912, i, 946; 1913, i, 249, 498, 1045; 1914, i, 1125; 1915, i, 382, 501; 1916, i, 413, 596, 711, 792). W. G.

New Hydrazones of some Monosaccharides (*p*-Tolylhydrazones of *l*-Arabinose, Rhamnose, Fucose, *d*-Mannose, and *d*-Galactose). A. W. van der Haar (*Rec. trav. chim.*, 1917, **36**, 346—351).—The following *p*-tolylhydrazones were prepared by warming the sugar and *p*-tolylhydrazine together in alcoholic solution. They are best crystallised from alcohol. l-*Arabinose*-p-*tolylhydrazone*, colourless, prismatic needles, m. p. 160°; *rhamnose*-p-*tolylhydrazone*, colourless leaflets, m. p. 166°; d-*mannose*-p-*tolylhydrazone*, colourless, rhomboidal plates, m. p. 190—191°; *fucose*-p-*tolylhydrazone*, long, colourless needles, m. p. 169°; d-*galactose*-p-*tolylhydrazone*, colourless, prismatic batons, m. p. 168°. Microphotographs of the crystals are given in the original. These *p*-tolylhydrazones are less soluble than the corresponding phenylhydrazones. Crystalline *p*-tolylhydrazones could not be obtained from xylose, *d*-fructose, or dextrose. W. G.

Product of Deflagration of Cellulose Nitrate. Eligio Trapani (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 332—334).—If a small quantity of a smokeless nitrocellulose powder, such as ballistite, cordite, or one based on cellulose nitrate alone, is carefully heated until it deflagrates, a pungent odour resembling that of formaldehyde is observable. Further, if the cold residue is treated with water and with sodium carbonate to neutralise the nitrous acid formed, the liquid obtained gives with phenylhydrazine hydrochloride and sodium nitroprusside the blue coloration characteristic of the presence of formaldehyde. The formaldehyde may be derived from the residue, $\cdot CH(OH)\cdot CH_2\cdot OH$, possibly existing in the cellulose nitrate or from some analogous chain formed in an early stage of the decomposition as a result of processes of denitration. Hydroxypyruvic acid constitutes one of the thermal decomposition products of cellulose nitrate, and this may yield formaldehyde by further degradation. The presence of formaldehyde is also probably related to that of carbon monoxide and hydrogen, which are formed on explosion of cellulose nitrate. T. H. P.

Aliphatic Hydroxylammonium Salts and Hydroxamic Acids with Halogen Substituents. Lauder William Jones and Louis F. Werner (*J. Amer. Chem. Soc.*, 1917, **39**, 413—422).—When chloro-, dichloro-, or trichloro-acetic acid is gradually added in the molten state to the calculated quantity of hydroxylamine at 0° and the mixture thoroughly stirred, the corresponding hydroxylammonium salt is obtained. *Hydroxylammonium chloroacetate* has m. p. 124—125°; the *dichloroacetate*, m. p. 116—116·5° (decomp.); and the *trichloroacetate*, m. p. 133—134°. When these chloroacetates are heated to their melting points variable amounts of the corresponding hydroxamic acids are formed, but owing to their instability at these temperatures the method is impracticable for preparing these hydroxamic acids. With bromo- and iodoacetic acids the halogens are so readily replaceable that the hydroxylammonium salts of these acids could not be obtained in the pure state.

Chloroacethydroxamic acid, m. p. 92—93°, is readily obtained by the addition of hydroxylamine to an alcoholic solution of ethyl chloroacetate. It gives an *acetyl* derivative, m. p. 85—86°; a white *sodium* salt, which when heated explodes with a yellow flame; a white *silver* salt, which soon decomposes, giving metallic silver; and a green *basic copper* salt, $C_4H_6O_5N_2Cl_2Cu_2$. The free acid when kept for four days is spontaneously converted into an *isomeride*, m. p. 108—108·5°, which gives an *acetyl* derivative, m. p. 67°.

When ethyl bromoacetate is added to a cold alcoholic solution of hydroxylamine, in a few minutes "basic" hydroxylammonium bromide, $[NH_2(OH)]_2HBr$, m. p. 110°, separates. A hydroxamic acid is also formed, but cannot be isolated. If the "basic" hydroxylammonium bromide is not removed, a further reaction occurs, and a *compound*, $C_8H_{15}O_5N$, m. p. 65°, is obtained, which the authors consider is a $\beta\beta$-disubstituted hydroxylamine, $HO{\cdot}N(CH_2{\cdot}CO_2Et)_2$. A similar reaction occurs with hydroxylamine and ethyl iodoacetate, the same compound, m. p. 65°, being obtained.

Bromoacethydroxamic acid, m. p. 103°, was finally prepared by mixing bromoacetyl bromide with hydroxylammonium chloride in aqueous solution containing sodium carbonate. The acid was separated as its green *basic copper* salt. *Iodoacethydroxamic acid*, m. p. 107·5° (corr.), was similarly prepared from iodoacetyl chloride and gave a dark green, normal *copper* salt. W. G.

Isomerism of the Polypeptides. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1917, **99**, 54—66).—The author gives formulæ for calculating the number of possible isomeric polypeptides containing amino-acids, of which some are alike and others different. The effects of the introduction of the diamino-acids and of cystine are taken into account, and, in simple cases, the influence of optical isomerism is dealt with. Fischer's octadecapeptide (A., 1907, i, 485), for instance, has 816 possible isomerides, whilst a complex polypeptide or protein containing 30 amino-acids, of which 5 are glycine, 4 alanine, 3 leucine, 3 lysine, 2 tyrosine, 2 phenylalanine, and the remaining 13 are other amino-acids, has no fewer than $1{\cdot}28 \times 10^{27}$ possible isomerides. The latter calculation is based on the assumption that the amino-acids are combined only in the simplest possible way, such as occurs between mono-aminomonocarboxylic acids. H. W. B.

The Nitrogenous Pigments of Molasses. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 298—306).—When dried molasses is extracted with alcohol, there remains undissolved a small percentage of non-saccharine substances which contain about 94% of the total pigment and 10% of the nitrogen of molasses. The question whether any of the nitrogen is present in a highly coloured compound naturally presents itself, and so the author has separated the residue into various fractions. One of them apparently contains a fairly definite substance which is precipitated by lead

acetate, is soluble in alcoholic hydrogen chloride solution, but not in ether, and contains 7·1—7·3% of nitrogen and about 0·2—0·3% of ash. It seems to be a product of the condensation of amino-acids with sugars, and is designated *fuscazinic acid.* The alkali salts of this account for about half of the colour of molasses.

J. C. W.

Action of Pyridine and of Piperidine on certain Organic Sulphur Compounds. III. M. RAFFO and O. BALDUZZI (*Gazzetta*, 1917, **47**, i, 65—73. Compare A., 1915, i, 86).—Just as when treated with mercuric oxide, thiocarbamide also loses sulphur when its pyridine solution is boiled, but in this case the final product is guanidine thiocyanate, which undergoes change with extreme readiness and could not be analysed; hydrogen sulphide is also formed, together with a compound regarded as ammonium trithiocarbonate.

When a pyridine solution of thioaminophenol is boiled, hydrogen sulphide is liberated and diaminophenyl sulphide formed:

$$2SH\cdot C_6H_4\cdot NH_2 \longrightarrow H_2S + S(C_6H_4\cdot NH_2)_2.$$

Under similar treatment, thioacetanilide yields hydrogen sulphide and acetanilide, the formation of the latter being apparently due to the presence of water in the pyridine used:

$$C_6H_4\cdot NH\cdot CS\cdot CH_3 + H_2O = C_6H_4\cdot NHAc + H_2S.$$

The desulphurising action of pyridine is not exclusive to this base. When a solution of diphenylthiocarbamide in piperidine is boiled in a reflux apparatus, hydrogen sulphide is evolved, and unstable, white needles, which apparently consist of piperidine hydrosulphide, form in the condenser; if the boiling is continued, the final products obtained are aniline, triphenylguanidine, and the piperidine derivative, $C_5H_{10}N\cdot CS\cdot SH,C_5H_{11}N$. T. H. P.

Investigations in the Cyanic Acid Series. EINAR BIILMANN and JOHANNE BJERRUM (*Ber.*, 1917, **50**, 503—510).—The molecular complexity of cyanurates in the gaseous state, the isomerism of cyanurates and *iso*cyanurates, and the action of phosphoric oxide on urethanes are discussed.

Trimethyl cyanurate is termolecular in the state of vapour, as measured by Victor Meyer's method in a bath of boiling benzophenone. At the boiling point of sulphur it suffers partial decomposition, but even so the volume of vapour does not indicate that much depolymerisation has taken place.

When silver cyanurate is treated with alkyl iodides in excess, *iso*cyanurates are formed as well as cyanurates. Some light is thrown on this reaction by the fact that in certain cases it has been possible to convert a cyanurate into an *iso*cyanurate by heating it with an alkyl haloid. It appears that the alkyl haloid is attached to the nitrogen atoms, and that the alkyl radicles already linked to oxygen are then ejected in combination with the halogen atoms. Thus, trimethyl cyanurate yields the *iso*cyanurate when heated with methyl iodide, and tribenzyl *iso*cyanurate when boiled with benzyl bromide. True *tribenzyl cyanurate*,

$$(C_6H_5\cdot CH_2\cdot O\cdot CN)_3,$$

m. p. 102—103° (from sodium benzyloxide and cyanuric chloride), also yields the *iso*cyanurate when heated with benzyl bromide.

When carbamates are heated with phosphoric oxide, they might be expected to yield cyanates, thus: $RO{\cdot}CO{\cdot}NH_2 \longrightarrow RO{\cdot}CN$. They give allophanates, however, according to the scheme: $2RO{\cdot}CO{\cdot}NH_2 = RO{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + R{\cdot}OH$, ethyl and methyl allophanates being most readily obtained from the corresponding carbamates. Xanthamide yields a small quantity of ethyl dithioallophanate, thus: $OEt{\cdot}CS{\cdot}NH_2 \longrightarrow OEt{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, but also suffers rearrangement into ethyl thiolurethane, and so gives ethyl thiocyanate as well, thus: $SEt{\cdot}CO{\cdot}NH_2 \longrightarrow SEt{\cdot}CN$.

In the hope of transforming ethyl nitrite into nitroethane by means of ethyl iodide, so as to give a similar explanation to the production of these isomerides by the action of ethyl iodide on silver nitrite, the reagents were heated in a sealed tube, but a violent explosion occurred when the cold tube was opened.

J. C. W.

New Fulminates and Azides. LOTHAR WÖHLER and F. MARTIN (*Ber.*, 1917, **50**, 586—596).—Some new fulminates have been obtained by the interaction of mercury or silver fulminate and the amalgam of the particular metal in dry methyl alcohol, the salt being precipitated from the solution by means of ether, and all the operations being conducted in an atmosphere of hydrogen.

Cadmium fulminate, $Cd(CNO)_2$, is a white powder which is quite stable when dry, but readily decomposed by water, in which it is very soluble. It retains about 1% of methyl alcohol tenaciously. It is one of the most violent explosives, and is nearly as sensitive to shock and heat as mercury fulminate. *Thallous fulminate* becomes superficially yellow in the light, and is very sensitive to moisture. It is the most susceptible of all known fulminates to shock and increased temperature, but the heat of detonation is not high, and so its explosion is not so violent. *Cuprous fulminate* is insoluble in water, and so may be prepared in aqueous media. It is pale grey (probably white; compare cuprous chloride) and is almost as violently explosive as cadmium fulminate, although not so sensitive to shock.

The preparation of mercury fulminate, and of the amalgams required for the above experiments, and the analysis of the salts are described. Details as to the value of these fulminates in explosives technology are being published elsewhere.

Some new azides have also been prepared, by shaking together finely divided, dry metallic carbonates or basic azides with an ethereal solution of azoimide until a portion of the solid is found to be completely soluble in water. *Nickel azide* is a sandy, green powder which absorbs water and holds it (about 13%) tenaciously; it is very soluble in water, but soon suffers hydrolysis. It is very sensitive to pressure, even gentle rubbing causing a most violent explosion. *Cobalt azide* is still more explosive, and is even more

dangerous than lead or silver azides. The ethereal liquid left from the preparation is reddish-brown and apparently contains a complex cobaltihydrazoic acid, for silver nitrate gives a brown precipitate instead of white silver azide. *Zinc azide* is a white, sandy powder which is very hygroscopic, and therefore usually obtained with associated water. It is readily hydrolysed, but is no more explosive than the alkaline earth azides. *Manganous azide* can only be obtained from the known basic azide. It is also white, hygroscopic, and easily hydrolysed, and explodes more violently than the zinc salt, but less so than the cobalt salt. *Ferric azide* has been obtained in very dark brown, hygroscopic leaflets by evaporating the solution formed when dry ferric sulphate and sodium azide are shaken with dry methyl alcohol. The well-known deep red colour of the solution of ferric azide, the formation of sodium azide by the action of nitrous oxide on sodamide, and of sodium thiocyanate by the action of carbon disulphide on sodamide, and the explosive nature of fulminates and azides, are commented on, in support of Thiele's formula for azoimide, the acids being represented thus: HN:N:N, HS·C:N, HO·N:C. Chromium hydroxide gives a very dark green, hygroscopic *complex*, probably of the formula $[Cr(N_3)_3OH]H$.

The heats of detonation in calories per gram of the fulminates and azides are given in the following table:

	Azides.	Fulminates.
Ag	452	470
Pb	364	—
Cu′	582	508
Hg′	266	—
Cd	558	470
Tl′	232	223
Ni	656	—
Zn	360	—
Mn″	676	—
Ca	625	—
Sr	295	—

J. C. W.

Organo-lead Compounds. VII. Lead Tetra-alkyls with Secondary Alkyl Radicles, and their Behaviour towards Halogens. Gerhard Grüttner and Erich Krause (*Ber.*, 1917, **50**, 574—580. Compare A., 1916, i, 684, 799, 800; this vol., i, 256, 257).—Lead tetra-alkyls containing one or two secondary alkyl radicles can be obtained quite readily by the action of the magnesium *sec.*-alkyl haloids on lead alkyl mono- or di-haloids. The attachment of lead to a secondary carbon atom is much weaker than to a primary, and therefore the new compounds differ in important respects from the many lead tetra-alkyls with normal radicles which have already been described. In the first place they are not stable in the air, but soon deposit flocculent products. Then the secondary radicle is expelled by bromine at $-75°$ with great ease, even before a lighter normal group. If two such groups are present, both are expelled, whereas in the case of

normal alkyl radicles only one is removed at this temperature. *Lead tetra*iso*propyl*, obtained by the action of magnesium *iso*propyl chloride on lead chloride, has m. p. $-53\cdot5°$ (corr.), b. p. 120°/14 mm., D_4^{12} 1·4578, n_{H_α} 1·52102, n_D 1·52600, n_{H_β} 1·53938, n_{H_γ} 1·5110, at 12°. *Lead trimethyl*iso*propyl* has b. p. 75°/60 mm., D_4^{20} 1·7403, n_{H_α} 1·5042, n_D 1·5095, n_{H_β} 1·5223, n_{H_γ} 1·5335°, at 20°. *Lead dimethylethyl*iso*propyl* has b. p. 61·2°/15 mm., $D_4^{20\cdot6}$ 1·6968, n_{H_α} 1·50812, n_D 1·51327, n_{H_β} 1·52614, n_{H_γ} 1·53731, $n_F - n_C$ 0·01801, at 20·6°. *Lead dimethylethyl*-sec.-*butyl*, $PbMe_2Et\cdot CHMeEt$, has b. p. 75°/14 mm., D_4^{21} 1·6322, n_D^{21} 1·5140, $n_F - n_C$ 0·01711. *Lead dimethylethyl*-sec.-*amyl*, $PbMe_2Et\cdot CHMePr$, has b. p. 90°/15 mm., D_4^{20} 1·5669, n_{H_α} 1·50676, n_D 1·51139, n_{H_β} 1·52341, n_{H_γ} 1·53401, at 20°. *Lead triethyl*iso*propyl* has b. p. 90°/13 mm., D_4^{20} 1·5812, n_{H_α} 1·5131, n_D 1·5181, $n_F - n_C$ 0·01773, $n_G - n_C$ 0·02884, at 20°. *Lead triethyl*-sec.-*butyl* has b. p. 103°/13 mm., D_4^{15} 1·5360, n_{H_α} 1·51600, n_D 1·52088, n_{H_β} 1·53310, n_{H_γ} 1·54390, at 15°, $n_F - n_C$ 0·01703. *Lead diethyl*-n-*propyl*iso*propyl* has b. p. 107°/17 mm., $D_4^{22\cdot1}$ 1·5336, n_{H_α} 1·51047, n_D 1·51524, n_{H_β} 1·52766, n_{H_γ} 1·53842, at 22·1°. *Lead diethyldi*iso*propyl* has b. p. 95·5°/14 mm., $D_4^{15\cdot9}$ 1·5358, n_{H_α} 1·51375, n_D 1·51870, n_{H_β} 1·53129, n_{H_γ} 1·54245, at 15·9°. *Lead diethyl*-n-*propyl*-sec.-*butyl* has b. p. 115·5°/14·5 mm., $D_4^{20\cdot1}$ 1·4962, n_{H_α} 1·51235, n_D 1·51698, n_{H_β} 1·52896, n_{H_γ} 1·53939 at 20·1°. *Lead triethyl*-sec.-*amyl* has b. p. 121°/17 mm., D_4^{21} 1·4906, n_{H_α} 1·51065, n_D 1·51537, n_{H_β} 1·52717, n_{H_γ} 1·53712, at 21°. *Lead dimethyl*-sec.-*butyl*iso-*amyl*, $CHMe_2\cdot CH_2\cdot CH_2\cdot PbMe_2\cdot CHMeEt$, has b. p. 111·5—112·5°/14 mm., D_4^{22} 1·4709, n_{H_α} 1·50125, n_D 1·50571, n_{H_β} 1·51686, n_{H_γ} 1·52675, at 22°. *Lead diethyl*-n-*propyl*-sec.-*amyl* has b. p. 121°/12 mm., $D_4^{19\cdot4}$ 1·4554, n_{H_α} 1·50948, n_D 1·51303, n_{H_β} 1·52551, n_{H_γ} 1·53571, at 19·4°.

All the densities are reduced to vacuum standard. J. C. W.

Cracking of an Aromatic Base Oil. The Temperature Factor at Constant Rate under Pressure. GUSTAV EGLOFF and ROBERT J. MOORE (*J. Ind. Eng. Chem.*, 1917, **9**, 40—42).—Solvent naphtha was subjected to thermal decomposition in a steel tube at temperatures of 500°, 600°, 650°, 700°, 750°, and 800° under a pressure of 11 atmospheres and a rate of flow of 15 gallons per hour. The highest yields of benzene in the recovered oil were obtained at the higher temperatures, with a maximum of 42·5% at 800°. The maximum yield of toluene was 39·9% at 750°, but as at the higher temperatures the percentage of recovered oil rapidly falls, the actual yield of toluene is the greater when calculated on the naphtha used, namely, 20·6% at 750°, as against 15·9% of benzene at 800°. The mechanism of the reaction is one of demethylation, similar to that produced by the action of aluminium chloride on alkylbenzene derivatives. Compared with the yields of benzene and toluene obtained by the cracking of paraffin and naphthene oils, the results obtained with solvent naphtha indicated that it is the most satisfactory oil to use for the production of these hydrocarbons, the benzene being 140% and the toluene 350% in excess of that obtained from the former oils. G. F. M.

Molecular Organic Compounds. MICHELE GIUA (*Gazzetta*, 1917, **47**, i, 74—86. Compare A., 1916, i, 266).—The points discussed in this paper comprise the historical development of the idea of molecular compounds, the nature and classification of molecular organic compounds, and labile molecular compounds.

T. H. P.

[Preparation of Diphenyl.] A. J. GRANT and C. JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 933—937).—See this vol., ii, 317.

Formation of Aniline from Ammonia and Benzene at High Temperatures, and in the Presence of Contact Catalysts. J. P. WIBAUT (*Ber.*, 1917, **50**, 541—546).—Meyer and Tanzen have shown that a small yield of aniline can be obtained by passing a mixture of benzene and ammonia through a tube heated at 550°, the reaction being reversible (A., 1913, i, 1294). Sabatier and Senderens have also shown that the reverse change, the conversion of aniline into benzene and ammonia by the action of hydrogen, takes place readily at 250° in the presence of nickel, and so the author has thought it to be of interest to find, if possible, a catalyst for the forward change.

Contrary to Meyer and Tanzen's experience, he finds that no appreciable amount of aniline is formed in a porcelain tube below 700° unless reduced iron, nickel, or copper is present. Even then the yield of aniline is very minute. The best result was obtained by passing a stream of ammonia through benzene at 75°, and then through an iron tube about 60 cm. long packed with reduced nickel, iron, and asbestos, heated at 550—560°, when 0·16 gram of acetanilide was produced from the 200 grams of condensed vapour.

J. C. W.

Action of Aromatic Amines on Aliphatic Acids. E. DE'CONNO (*Gazzetta*, 1917, **47**, i, 93—132).—A number of anilides of higher aliphatic acids have been prepared by heating the acid (1 mol.) with the aromatic amine (1 mol.) for five hours at 230° in a sealed tube freed from air by means of a mercury pump (compare A., 1916, i, 788). The anilides thus obtained are crystalline and melt to dark yellow liquids, with the exception of those of linolenic acid, which are liquid at the ordinary temperature. In all cases they are completely hydrolysed when heated in a sealed tube at 150° with concentrated hydrochloric acid. All the amides yet prepared distil unaltered under a pressure of 10 mm., and the increment of the boiling point in a homologous series is at least 10°, so that fractional distillation in a vacuum should result in sharp separation of the constituents of a mixture of such amides.

Myristoanilide, $C_{13}H_{27}\cdot CO\cdot NHPh$ (compare Masino, A., 1880, 460), forms slender needles, m. p. 81·5°, b. p. 113°/10 mm.

Palmitoanilide, $C_{15}H_{31}\cdot CO\cdot NHPh$ (compare Dellschaft, A., 1902, i, 142; Hell and Jordanoff, A., 1891, 820, 821), forms long, hard, silky needles, m. p. 88·5°, b. p. 132·5°/10 mm.

Stearoanilide, $C_{17}H_{35}\cdot CO\cdot NHPh$ (compare Pébal, *Annalen*, 1854, **91**, 138; Claus and Häfelin, A., 1897, i, 187), forms radiating masses of slender, shining, white needles, m. p. 88°, b. p. 153·5°/10 mm.

Arachoanilide, $C_{19}H_{39}\cdot CO\cdot NHPh$ (compare Baczewski, A., 1897, i, 11), forms long, white, matted needles, m. p. 91·5°, b. p. 172°/10 mm.

Oleoanilide, $C_{17}H_{33}\cdot CO\cdot NHPh$, forms nacreous masses of slender, shining, colourless needles, m. p. 41°, b. p. 143·5°/10 mm. Erucoanilide, $C_{21}H_{41}\cdot CO\cdot NHPh$ (compare Reimer and Will, A., 1887, 233), forms masses of minute, shining needles, m. p. 55°, b. p. 181°/10 mm. *Linolenoanilide*, $C_{17}H_{29}\cdot CO\cdot NHPh$, forms a faint yellow, neutral, oily, limpid liquid.

Myristo-p-*toluidide*, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous flakes composed of long, slender needles, m. p. 84°, b. p. 121·5° / 10 mm. Palmito-*p*-toluidide, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_4Me$ (compare Claus and Häfelin, *loc. cit.*), forms nacreous masses of long, silky needles, m. p. 93·5°, b. p. 140°/10 mm. *Stearo*-p-*toluidide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous masses of slender, white needles, m. p. 95·5°, b. p. 161·5°/10 mm. *Aracho*-p-*toluidide*, $C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_4Me$, forms long, white needles, m. p. 96°, b. p. 189·5°/10 mm. *Oleo*-p-*toluidide*,

$$C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_4Me,$$

forms felted masses of minute, shining needles, m. p. 42·5°, b. p. 156·5°/10 mm. *Eruco*-p-*toluidide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_4Me$, forms nacreous masses of minute, shining needles, m. p. 57·5°, b. p. 192·5°/10 mm. *Linoleno*-p-*toluidide*,

$$C_{17}H_{29}\cdot CO\cdot NH\cdot C_6H_4Me,$$

forms a clear, almost colourless oil.

Myristo-m-*xylidide*, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms mammillary masses of long, soft needles, m. p. 93°, b. p. 127·5°/10 mm. *Palmito*-m-*xylidide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms mammillary masses of soft, almost colourless needles, m. p. 97·5°, b. p. 148°/10 mm. Stearo-*m*-xylidide, $C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_3Me_2$ (compare Claus and Häfelin, *loc. cit.*), forms minute, white needles, m. p. 102°, b. p. 159·5°/10 mm. *Aracho*-m-*xylidide*, $C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms masses of shining, white needles, m. p. 99°, b. p. 181·5°/10 mm. *Oleo*-m-*xylidide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms masses of minute, shining, colourless needles, m. p. 59·5°, b. p. 167·5°/10 mm. *Eruco*-m-*xylidide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_3Me_2$, forms gum-like masses of matted, minute needles, m. p. 68·5°, b. p. 190°/10 mm. *Linoleno*-m-*xylidide*, $C_{17}H_{29}\cdot CO\cdot NH\cdot C_6H_3Me_2$, is an oily, almost colourless liquid. *Myristo*-p-*hydroxyanilide*, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms minute, shining, colourless needles, m. p. 113°, b. p. 206°/10 mm. *Palmito*-p-*hydroxyanilide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms matted masses of minute, shining needles, m. p. 131°, b. p. 225·5°/10 mm. *Stearo*-p-*hydroxyanilide*,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_4\cdot OH,$$

forms long, colourless needles, m. p. 132°, b. p. 239·5°/10 mm.

Aracho-p-*hydroxyanilide*, $C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms matted masses of long, white needles, m. p. 115°, b. p. 259°/10 mm. *Oleo*-p-*hydroxyanilide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms slender, white needles, m. p. 80°, b. p. 251·5°/10 mm. *Eruco*-p-*hydroxyanilide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, forms silver-white crusts of minute, shining needles, m. p. 114°, b. p. 282°/10 mm.

Myristo-p-*methoxyanilide*, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, forms shining, colourless needles, m. p. 101·5°, b. p. 215·5°/10 mm. *Palmito*-p-*methoxyanilide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, forms long, colourless needles, m. p. 108°, b. p. 238°/10 mm. *Stearo*-p-*methoxyanilide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, forms minute, white needles, m. p. 104°, b. p. 259·5°/10 mm. *Aracho*-p-*methoxyanilide*,

$$C_{19}H_{39}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe,$$

forms long, white needles, m. p. 106°, b. p. 281·5°/10 mm. *Oleo*-p-*methoxyanilide*, $C_{17}H_{33}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, forms minute, colourless needles, m. p. 67°, b. p. 262°/10 mm. *Eruco*-p-*methoxyanilide*, $C_{21}H_{41}\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, forms minute, shining, colourless needles, m. p. 85°, b. p. 287·5°/10 mm.

Myristo-p-*ethoxyanilide*, $C_{22}H_{37}O_2N$, forms minute, silky needles, m. p. 108°, b. p. 228·5°/10 mm. *Palmito*-p-*ethoxyanilide*, $C_{24}H_{41}O_2N$, forms minute, translucent scales, m. p. 109°, b. p. 250°/10 mm. *Stearo*-p-*ethoxyanilide*, $C_{26}H_{45}O_2N$, forms shining, white needles, m. p. 110°, b. p. 269·5°/10 mm. *Aracho*-p-*ethoxyanilide*, $C_{28}H_{49}O_2N$, forms minute, shining, white needles, m. p. 111°, b. p. 290°/10 mm. *Oleo*-p-*ethoxyanilide*, $C_{26}H_{43}O_2N$, forms minute, shining, colourless needles, m. p. 72°, b. p. 265·5°/10 mm. *Eruco*-p-*ethoxyanilide*, $C_{30}H_{51}O_2N$, forms small, silky chips, m. p. 87°, b. p. 288°/10 mm.

Myristo-α-naphthalide, $C_{13}H_{27}\cdot CO\cdot NH\cdot C_{10}H_7$, forms masses of slender needles, m. p. 110°, b. p. 162·5°/10 mm. *Palmito-α-naphthalide*, $C_{15}H_{31}\cdot CO\cdot NH\cdot C_{10}H_7$, forms radiating masses of hard, silky needles, m. p. 112·8°, b. p. 182°/10 mm. *Stearo-α-naphthalide*, $C_{28}H_{43}ON$, forms mammillary masses of short, slender, white needles, m. p. 110·8°, b. p. 205°/10 mm. *Aracho-α-naphthalide*, $C_{30}H_{47}ON$, forms minute needles, m. p. 99°, b. p. 221·5°/10 mm. *Oleo-α-naphthalide*, $C_{28}H_{41}ON$, forms minute needles, m. p. 60°, b. p. 190·5°/10 mm. *Eruco-α-naphthalide*, $C_{32}H_{49}ON$, forms masses of minute, shining needles, m. p. 73°, b. p. 230°/10 mm.

Myristo-β-naphthalide, $C_{24}H_{35}ON$, forms mammillary masses of long, slender needles, m. p. 108°, b. p. 179°/10 mm. *Palmito-β-naphthalide*, $C_{26}H_{39}ON$, forms mammillary masses of small, acicular crystals, m. p. 109°, b. p. 198·5°/10 mm. *Stearo-β-naphthalide*, $C_{28}H_{43}ON$, forms nacreous masses of slender, white needles, m. p. 109°, b. p. 220·5°/10 mm. *Aracho-β-naphthalide*, $C_{30}H_{47}ON$, forms shining, white needles, m. p. 112°, b. p. 239°/10 mm. *Oleo-β-naphthalide*, $C_{28}H_{41}ON$, forms shining masses of nacreous scales, m. p. 169·2°, b. p. 215·5°/10 mm. *Eruco-β-naphthalide*, $C_{32}H_{49}ON$, forms shining, colourless needles, m. p. 87°, b. p. 247·5°/10 mm.

Myristo-p-*phenylenediamide*, $C_6H_4(NH\cdot CO\cdot C_{13}H_{27})_2$, forms

minute, pale grey needles, m. p. 162·5°, b. p. 186·5°/10 mm. *Palmito*-p-*phenylenediamide*, $C_{38}H_{68}O_2N_2$, forms short, almost colourless, shining needles, m. p. 181·5°, b. p. 208°/10 mm. *Stearo*-p-*phenylenediamide*, $C_{42}H_{76}O_2N_2$, forms minute, white needles, m. p. 179·5°, b. p. 229·5°/10 mm. *Aracho*-p-*phenylenediamide*, $C_{46}H_{84}O_2N_2$, forms minute needles, m. p. 139·8°, b. p. 250°/10 mm. *Oleo*-p-*phenylenediamide*, $C_{42}H_{72}O_2N_2$, forms minute needles, m. p. 158·7°, b. p. 224·5°/10 mm. *Eruco*-p-*phenylenediamide*, $C_{50}H_{88}O_2N_2$, forms minute, grey needles, m. p. 151°, b. p. 263°/10 mm. T. H. P.

Polymorphism of 2 : 6-Dinitro-4-toluidine. I. and II. E. Artini (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 392—400, 420—424).—This compound, prepared by Körner and Contardi by reducing 2 : 4 : 6-trinitrotoluene with ammonium sulphide, exists in four distinct crystalline phases, with the following properties.

The δ-modification, obtained by slow evaporation of a cold saturated solution in a mixture of ether and alcohol, forms prismatic crystals of the rhombic system (? bipyramidal class), $a : b = 0·7935 : 1$, D 1·524, showing marked pleochroism.

The γ-phase, which is easily obtained by evaporation of cold saturated solutions in ethyl acetate or acetone, either alone or mixed with alcohol, forms crystals of varying habit, but mostly short and stout and belonging to the pinacoidal class of the triclinic system, $a : b : c = 0·8389 : 1 : 2·1764$, $\alpha = 93°26'$, $\beta = 89°00'$, $\gamma = 89°33'$, D 1·497; twinning is frequent and pleochroism evident.

The β-form, which is often obtained with the γ-modification from ethyl acetate or acetone and is also deposited on very slow cooling of a boiling alcoholic solution, forms rhombic crystals of the bipyramidal class, $a : b : c = 0·8557 : 1 : 1·1119$, D 1·495, and shows distinct pleochroism.

In spite of their different degrees of symmetry, the γ- and β-modifications are markedly similar in external form, and also exhibit various morphological and physical relations and frequently occur associated.

The δ-phase is metastable, at any rate as far as temperatures a few degrees below 0°, and if it is deposited in a flask from a mixture of ether and alcohol and, when the crystallisation has proceeded sufficiently far, the flask is stoppered, the yellow δ-needles gradually pass into solution and are replaced by the triclinic γ-form. The latter is the most stable at the ordinary or a lower temperature and the β-phase is metastable towards the γ-phase at the ordinary temperature.

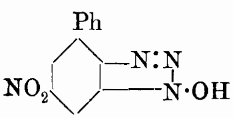
The fourth or α-phase forms pale orpiment-yellow crystals and arises when either of the preceding modifications is heated at 148°, its region of stability extending only from 148° to 173°, the melting point. When cooled below 148° it undergoes immediate transformation into the β-phase.

The conditions of equilibrium between the different phases are represented graphically. T. H. P.

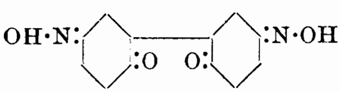
Some New Derivatives of Diphenyl. W. Borsche and B. G. B. Scholten (*Ber.*, 1917, **50**, 596—611).—Now that *o*-hydroxy- and *oo'*-dihydroxy-diphenyl are commercial products, material has become available for a resumption of an investigation on diphenyl derivatives begun in 1900 (A., 1900, i, 24, 594).

Derivatives of o-*Hydroxydiphenyl.*—2-Phenylbenzoquinone-4-oxime, which was originally the precursor of the *o*-hydroxydiphenyl, is best obtained from this by the action of nitrous acid. It may be oxidised by alkaline potassium ferricyanide or hydrogen peroxide to 5-nitro-2-hydroxydiphenyl (*ibid.*, 594), and this converted by methylation into 5-*nitro*-2-*methoxydiphenyl*, pale yellow, friable needles, m. p. 95—96°. The latter can be obtained readily by the nitration of *o*-methoxydiphenyl (methylation of the phenol; b. p. 159—160°/18 mm.), but the free phenol yields almost exclusively 3:5-dinitro-2-hydroxydiphenyl, m. p. 203—204°. The phenol couples with benzenediazonium chloride, giving 2-*hydroxy*-5-*benzeneazodiphenyl*, yellow needles, m. p. 94—95°, and 2-*hydroxy*-3:5-*bisbenzeneazodiphenyl*, brown needles, m. p. 157°. The former azo-compound is readily reduced by sodium hyposulphite to 5-amino-2-hydroxydiphenyl, m. p. 201°.

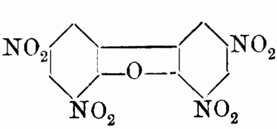
3:5-Dinitro-2-hydroxydiphenyl forms a *p-toluenesulphonate*, long, stout, yellow needles, m. p. 147—148°, and also 2-*chloro*-3:5-*dinitrodiphenyl*, yellow leaflets, m. p. 119°, when heated with *p*-toluenesulphonyl chloride and dimethylaniline (a reaction of *op*-dinitrophenols discovered by Ullmann and Nádai; A., 1908, i, 525). The *o*-chloro-derivative reacts with alcoholic ammonia at 100° to form 3:5-*dinitro*-2-*aminodiphenyl*, golden-yellow leaflets, m. p. 182°; with aniline, very sluggishly, to give 3:5-*dinitro*-2-*anilinodiphenyl*, bright red needles, m. p. 130°; and with hydrazine hydrate to yield 6-*nitro*-4-*phenylbenzazimin-ol* (annexed formula), which crystallises in yellow leaflets, decomp. 229°.



Derivatives of oo'-*Dihydroxydiphenyl.*—This phenol reacts with acetic acid and sodium nitrite to form 2:2'-*diphenyldiquinone*-4:4'-*dioxime* (annexed formula) as a dark yellow, microcrystalline powder which decomposes briskly at 227—228°. This may be reduced to 5:5'-diamino-2:2'-dihydroxydiphenyl, but the amine is more readily obtained by reducing 5:5'-bisbenzeneazo-2:2'-diphenol (Robertson and Brady, T., 1913, **103**, 1481) with sodium hyposulphite. The diamine yields the 2:2'-diphenyldiquinone, m. p. 196°, on oxidation.



3:5:3':5'-Tetranitro-2:2'-diphenol does not behave in the normal way on heating with *p*-toluenesulphonyl chloride and dimethylaniline. It yields 1:3:6:8-*tetranitrodiphenylene oxide* (annexed formula), which crystallises in lustrous, pale brown needles, m. p. 252·5°.



2:2'-Dimethoxydiphenyl yields 5:5'-*dinitro*-2:2'-*dimethoxydiphenyl*, slender,

yellow needles, m. p. 263°, when warmed with nitric (D 1·39) and glacial acetic acids, but when first sulphonated and then warmed with fuming nitric and sulphuric acids, it forms 3:5:3′:5′-*tetranitro-2:2′-dimethoxydiphenyl*, which crystallises in broad, yellow needles, m. p. 177—178°. The latter yields the well-known 1:3:6:8-tetranitrocarbazole, m. p. 268°, when heated with alcoholic ammonia at 140—150°, but this synthesis offers the first proof of the constitution of the compound.

Derivatives of pp′-*Dihydroxydiphenyl.*—3:5:3′:5′-Tetranitro-4:4′-dihydroxydiphenyl is obtained by adding concentrated nitric acid to diazotised benzidine and warming. It only forms a *di*-p-*toluenesulphonate*, yellow leaflets, m. p. 267° (decomp.), when treated by the above method of Ullmann and Nádai, no trace of the tetranitro-4:4′-dichlorodiphenyl being produced. Neither could any more than the known 2:2′-dinitro-compound be obtained by nitrating 4:4′-dichlorodiphenyl. The above ester is transformed by boiling aniline into 3:5:3′:5′-*tetranitro-4:4′-dianilinodiphenyl*, which crystallises in fiery-red needles, m. p. 271°.

Derivatives of mm′-*Dichlorodiphenyl.*—This oil yields 5:5′-dichloro-2:2′-dinitrodiphenyl when carefully warmed with fuming nitric acid, but 5:5′-*dichloro-2:4:2′:4′-tetranitrodiphenyl*, yellow leaflets, m. p. 189°, when warmed with a mixture of sulphuric and fuming nitric acids. The latter yields the 5:5′-*diamine*, reddish-brown crystals, m. p. 297°, and an additive *compound* of aniline and the 5:5′-dianilino-derivative, $C_{12}H_4(NHPh)_2(NO_2)_4,NH_2Ph$, stout, dark red needles, m. p. 215°. J. C. W.

The State of Saturation of Chromophores. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 630—637).—The author issues a warning against a false idea of the importance of the degree of unsaturation in connexion with colour theories. There is a tendency in some quarters (compare Ley, this vol., i, 261, and Lifschitz, *Zeitsch. wiss. Photochem.*, 1916, **16**, 101) to expect that a lowering of the intensity of colour would follow if the degree of unsaturation of the chromophore is lowered. Even when such difficulties are ignored as the question as to what "unsaturation" really means, what kind of unsaturation is authoritative in optical problems, why it is that ethylene is colourless whilst more saturated stilbene derivatives are coloured, why *m*-nitroaniline is coloured but *m*-dinitrobenzene colourless, why colourless aniline and almost colourless 1:3:5-trinitrobenzene should form a red compound, there are still, even within narrow limits, cases in which colour is actually enhanced when the degree of unsaturation is lessened.

It is known, for example, that the degree of saturation of an ethylene linking is raised by the proximity of a phenyl, carboxyl or carbethoxyl, or cyano-group in the order given, but in three cases the effect on the colour is quite the opposite to the expected one. In the series R·CH⁚CHPh, $R·CH⁚CPh·CO_2H$, R·CH⁚CPh·CN [$R=C_6H_3(OMe)_2$,2:5], the colours are white, pale greenish-yellow, and bright greenish-yellow; with the compounds of the same radicle, R·CH⁚CPh·CN, $R·CH⁚C(CN)·CO_2Et$, $R·CH⁚C(CN)_2$, the colours are greenish-yellow, lemon or orange-red (two forms), and

orange-yellow; whilst in the series of para-derivatives of dimethylaniline, R·CH:CHBz, R·CH:CPhBz, R·CH:CBz·CN,

R·CH:CPh·CN,

R·CH:C(CN)·CO_2Et, R·CH:$C(CN)_2$, the compounds are orange-red, chrome-yellow, brick-red, lemon-yellow, orange, and brick-red respectively.

It is therefore emphasised that whilst "unsaturation" is a factor which confers chromophoric properties on atomic groups, it is in no sense the factor which determines the degree of the chromophoric activity.

Some new compounds have been prepared [with KARL BURR, EMIL MEYER, and ADOLF JEUTTER]. *ω-Nitro-2:5-dimethoxystyrene*, from the dimethoxybenzaldehyde and nitromethane, forms long, orange-red, fluorescent needles, m. p. 118°. *2:5-Dimethoxy-β-nitro-Δ^{α}-propenylbenzene*, NO_2·CMe:CH·$C_6H_3(OMe)_2$, from nitroethane, crystallises in slender, orange-yellow needles, m. p. 75°. *ω-Nitro-2:5-dimethoxystilbene*, NO_2·CPh:CH·$C_6H_3(OMe)_2$, from phenylnitromethane, forms orange-yellow crystals, m. p. 124°. The colours in these cases are therefore lessened in intensity as the ethylene linking becomes more saturated.

2:5-Dimethoxy-α-phenylcinnamic acid, from the aldehyde and sodium phenylacetate and acetic anhydride, forms pale greenish-yellow crystals, m. p. 192°.

p-*Dimethylaminobenzylidenedeoxybenzoin*,

NMe_2·C_6H_4·CH:CPh·COPh,

crystallises in chrome-yellow needles, m. p. 167°. J. C. W.

Aminophenylethylcarbinol [β-Amino-α-phenylpropyl Alcohol]. AUGUST EBERHARD (*Arch. Pharm.*, 1917, **255**, 140—150).—In order to synthesise ephedrine or ψ-ephedrine, it is necessary to methylate β-amino-α-phenylpropyl alcohol. Preliminary work on this reaction has shown that much material will be required in order to obtain a pure product (Calliess, A., 1912, i, 365; Eberhard, A., 1915, i, 834). It is now found that the carbinol can best be prepared from α-aminopropiophenone by reduction with hydrogen in the presence of palladinised charcoal. The methylation of the hydramine will be described later, but some new derivatives have been obtained in the meantime and others revised.

β-Amino-α-phenylpropyl alcohol crystallises in flat needles, m. p. 101°, and yields the following compounds: a hydrochloride, m. p. 191°; two isomeric but not interchangeable aurichlorides (bundles of silky, yellow needles, m. p. 130°, and hard, yellowish-red rosettes, m. p. 172°); two platinichlorides (yellowish-red needles, with $2H_2O$, m. p. 187—188°, and anhydrous, brownish-red bundles, m. p. 196°); a benzoyl derivative, m. p. 142° (Behr-Bregowski, A., 1897, i, 460); and a *dibenzoyl* compound, OBz·CHPh·CHMe·NHBz, white flocks, m. p. 162°. J. C. W.

***p*-Lactylaminobenzoic Acid.** E. SALKOWSKI (*Ber.*, 1917, **50**, 637—641).—As another attempt to prepare a soluble, but physiologically active, derivative of ethyl *p*-aminobenzoate (compare A.,

1916, i, 815), the drug ("anæsthesine") has been converted into the lactyl derivative, by heating with an excess of lactic acid. The new ester is a brown syrup which is neither soluble nor possessed of anæsthetic properties. The free *p-lactylaminobenzoic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CHMe\cdot OH$, obtained by hydrolysis of the crude product or, better, by heating together the free acids, crystallises as a mass of woolly needles, m. p. 215°, and yields a white *silver*, and a microcrystalline *copper* salt. It gives no coloration with ferric chloride (distinction from *p*-aminobenzoic acid); it is gradually hydrolysed by boiling sodium hydroxide, but not by sodium carbonate. J. C. W.

Synthesis of Phloretin, and Preparation of the Nitriles of Phenolcarboxylic Acids. EMIL FISCHER and OSMAN NOURI (*Ber.*, 1917, **50**, 611—623).—The nitriles of phenolcarboxylic acids can be obtained by converting the acetyl compounds into the amides, dehydrating these with phosphorus chlorides, and finally removing the acetyl groups again by a mild hydrolysis. By such a means, phloretonitrile has been prepared and then converted into phloretin by Hoesch's new method for the synthesis of phenolic ketones (compare A., 1915, i, 820).

Phloretic acid (β-*p*-hydroxyphenylpropionic acid) is most conveniently obtained by the hydrolysis of phloridzin, and its esters by means of the alcohols and sulphuric acid. The ethyl ester has m. p. 43—44°, b. p. 193°/18 mm. (corr.); the *methyl* ester crystallises in large, thin tablets, m. p. 40—41° (corr.), b. p. 186—187°/17 mm. (corr.). The amide, m. p. 127—128°, is best obtained from the methyl ester. *Acetylphloretamide* (β-p-*acetoxyphenylpropionamide*) is formed by the action of acetic anhydride and pyridine on the amide; it crystallises in elongated, thin plates, m. p. 133—134° (corr.), and yields the corresponding *nitrile*, b. p. 170—175°/0·25 mm., when heated with chloroform and phosphoryl chloride. *Phloretonitrile* (β-p-*hydroxyphenylpropionitrile*) is obtained from this by hydrolysis with cold aqueous-alcoholic sodium hydroxide, in colourless prisms, m. p. 58—59°. When an ethereal solution of the acetylphloretonitrile and phloroglucinol is treated with hydrogen chloride in the presence of zinc chloride, condensation takes place as in Hoesch's method, and the intermediate ketone-imide salt can be hydrolysed to a mixture of free phloretin and its acetyl derivative. A further treatment with *N*-sodium hydroxide in the absence of air serves to decompose the acetate, and phloretin, $HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_2(OH)_3$, identical with the phloretin of phloridzin may be isolated.

Methyl *p*-coumarate, m. p. 139—140° (corr.), is converted into p-*coumaramide*, microscopic leaflets, m. p. 193—194° (corr.), and the *acetyl* derivative of this, m. p. 189—191° (corr.), into p-*acetoxycinnamonitrile*, m. p. 117—118° (corr.), and finally into p-*coumaronitrile*, long prisms, m. p. 138—139° (corr.), by the above methods.

Similarly, gallamide is transformed into the triacetate, *triacetylgallonitrile*, long needles or prisms, m. p. 129—130° (corr.), and

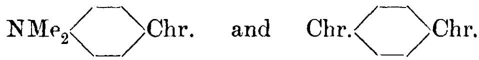
finally *gallonitrile*, which crystallises from water in very long needles, $1H_2O$, m. p. 223° (corr.). J. C. W.

Phenylpyruvic Acid. (MLLE.) R. HEMMERLÉ (*Ann. Chim.*, 1917, [ix], **7**, 226—276).—A full account of work of which a short description has appeared (compare A., 1916, i, 485). Certain new compounds are described, namely, *sodium phenylpyruvate*, $C_9H_7O_3Na,H_2O$; the *methyl* ester, m. p. 75°; the *ethyl* ester, m. p. 45°; and the *acetate*, m. p. 168°, of phenylpyruvic acid; the *acetate*, m. p. 125°, of benzylpyruvic acid; *methyl diphenyldipyruvate*, m. p. 101°; *ethyl diphenyldipyruvate*, m. p. 102°; the *keto-alcohol*, $CO_2H{\cdot}CO{\cdot}CHPh{\cdot}CHPh{\cdot}OH$, corresponding with α-keto-$\beta\gamma$-diphenylbutyrolactone (compare Erlenmeyer, A., 1904, i, 1015); *α-keto-β-phenylbutyrolactone*, m. p. 202°, and its *semicarbazone*, m. p. 220° (decomp.), and its *methyl ether*, m. p. 84°. W. G.

An Ethoxy-β-naphthoylpropionic Acid. M. GIUA (*Gazzetta*, 1917, **47**, i, 89—92. Compare A., 1914, i, 962).—The action of succinic anhydride on α-naphthyl ethyl ether in carbon disulphide solution and in the presence of aluminium chloride yields an *ethoxy-β-naphthoylpropionic acid*, $OEt{\cdot}C_{10}H_6{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which forms pale yellow needles, m. p. 198°, gives a greenish-yellow coloration with concentrated sulphuric acid, and yields *o*-phthalic acid on oxidation with alkaline permanganate solution; the acid is probably 5-ethoxy-β-2-naphthoylpropionic acid. Its *methyl* ester forms shining, white plates, m. p. 70—71°.

Methyl β-2-naphthoylpropionate (compare A., 1914, i, 962), $C_{15}H_{14}O_3$, forms white, prismatic crystals, m. p. 74°. T. H. P.

Chromophores with Auxochromic Functions. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 515—529).—The colour and fluorescence of a number of compounds of the two types:



(Chr. = chromophore) have been investigated. It is a well-known fact that *p*-dinitrobenzene is no more coloured than nitrobenzene, but that *p*-dimethylaminonitrobenzene, containing an auxochrome, is bright yellow. Certain cases of styryl derivatives have now been found, however, in which the association of two of these chromophores in compounds of the type II makes for the enhancement of colour over the monostyryl derivatives or even over the corresponding *p*-dimethylaminostyryl derivatives of type I. In these cases, therefore, the styryl complex exerts auxochromic functions; indeed, it sometimes happens that the auxochrome effect is more pronounced than that displayed by the *p*-dimethylamino-group. The chief argument, however, for the exertion of auxochrome activities by these chromophores is that the compounds display brilliant fluorescence, which is in accordance with the rule that the introduction of a second auxochrome in the para-position with respect to another makes for a strongly fluorescent di-derivative.

The following summary illustrates these points. The data refer to the solid compounds.

	$NMe_2\cdot C_6H_4\cdot$Chr.		Chr$\cdot C_6H_4\cdot$Chr.	
Chromophore.	Colour.	Fluorescence.	Colour.	Fluorescence.
$\cdot CH:CHPh$	White	Moderately strong greenish-blue	Pale yellow	Strong yellowish-green
$\cdot CH:CPh\cdot CN$	Lemon-yellow	Intense vivid greenish-yellow	Lemon-yellow	Intense yellow
$\cdot CH:C(CN)\cdot CO_2Et$.	Orange	Vivid orange	Pale greenish-yellow	Vivid yellowish-green
$\cdot CH:C(CN)_2$	Brick red	Strong orange-red	Yellow	Strong yellow
$\cdot CH:C(CN)\cdot COPh$..	Brick red	Vivid brick-red	Orange-yellow	Very faint yellow
$\cdot CH:C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$	Deep red	Moderate purple-red	Orange	Strong orange

Most of the compounds were obtained by the condensation of the appropriate aldehydes and methylene compounds.

[With ADOLF JEUTTER.]—p-*Distyrylbenzene*, $C_6H_4(CH:CHPh)_2$, is obtained by the action of terephthalaldehyde on magnesium benzyl chloride, the intermediate carbinol being deprived of the elements of water by heating with acetyl chloride and then alone at 270°. It forms pale yellow crystals, m. p. 258°. *ωω'-Dicyano*-p-*distyrylbenzene*, $C_6H_4(CH:CPh\cdot CN)_2$, yellow crystals, m. p. 242°, is obtained from terephthalaldehyde and benzyl cyanide. *Ethyl terephthalylidenedicyanoacetate*, $C_6H_4[CH:C(CN)\cdot CO_2Et]_2$, from terephthalaldehyde and ethyl cyanoacetate, forms pale greenish-yellow needles, m. p. 201°. *Terephthalylidenedimalononitrile*,

$$C_6H_4[CH:C(CN)_2]_2,$$

decomposes at 212°. *Terephthalylidenedicyanoacetophenone*, $C_6H_4(CH:CBz\cdot CN)_2$, has m. p. 224°. *Terephthalylidenedi-indandione* forms orange needles, m. p. above 300°.

Phenyl cyanostyryl ketone forms white crystals, m. p. 84°; *phenyl cyano*-p-*methoxystyryl ketone* crystallises in pale yellow needles, m. p. 104°; *phenyl cyano*-p-*dimethylaminostyryl ketone*, m. p. 162°, is brick-red, and forms a white salt with hydrogen chloride gas or solution; *phenyl cyano*-p-*nitrostyryl ketone* crystallises in pale yellow scales, m. p. 140°; p-*nitrobenzylideneindandione*,

$$NO_2\cdot C_6H_4\cdot CH:C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

forms greenish-yellow needles, m. p. 229°; *αδ-dicyano-αδ-dibenzoylbutadiene*, $CN\cdot CBz:CH\cdot CH:CBz\cdot CN$, from glyoxal and cyanoacetophenone, decomposes at 170—175°, and is white, whereas the terephthalylidene compound in which the $-CH:CBz\cdot CN$ chromophores are separated by the benzene nucleus is orange-yellow.

[With EMIL MEYER.]—p-*Dimethylamino-ω-cyanostilbene*,

$$NMe_2\cdot C_6H_4\cdot CH:CPh\cdot CN,$$

from benzyl cyanide and *p*-dimethylaminobenzaldehyde, forms yellow leaflets, m. p. 136°. Its fluorescence in diffused light or

β-rays is comparable in intensity with that of barium platinocyanide, but it is not sensitive to Röntgen rays. J. C. W.

Dextro-rotatory Menthyl Iodide. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1151—1156).—Gradual hydrolysis of crude menthyl chloride shows that the latter contains, besides the lævo-rotatory stable chloride, at least two unstable stereoisomerides with rotations of opposite signs; the menthyl bromide and iodide obtained by similar methods from menthol probably contain analogous secondary stereoisomerides. Menthyl bromide and iodide are sometimes obtained optically inactive or with a slight dextro-rotation, which may, however, be due to a small proportion of admixed menthene formed as a result of the instability of the menthyl haloid. The author has now succeeded in preparing a menthyl iodide with a pronounced dextro-rotation, which cannot be explained by admixture of menthene.

The method of preparation used was similar to that of Celikov (*ibid.*, 1904, **36**, 784). Menthyl acetate, b. p. 101—102°/15 mm., α_D $-73{\cdot}05°$ for 10 cm., prepared by boiling menthol with acetic anhydride, was dissolved in an equal volume of chloroform and the solution saturated with dry hydrogen iodide at $-20°$. The containing tube was then sealed and left at the ordinary temperature for five days. The resulting menthyl iodide, $C_{10}H_{19}I$, b. p. 122—123°/17 mm., D_4^0 1·3787, D_4^{20} 1·3586, exhibits a dextro-rotation which for three different preparations amounted to $+41{\cdot}2°$, $+35{\cdot}13°$, and $+37{\cdot}62°$ in a 10 cm. tube. The menthene obtained by boiling this menthyl iodide with alcoholic potassium hydroxide exhibits the same physical properties as that derived from lævo-rotatory menthyl haloids. The dimenthyl formed, together with menthene and menthane, when the dextro-rotatory menthyl iodide is boiled with sodium in ethereal solution, is a mixture of the same isomerides as are obtained from the ordinary haloid derivatives of menthol, but the crystalline dimenthyl is formed in comparatively small quantity.

Menthyl iodide has also been prepared, in the same way as from menthyl acetate, from menthyl hydrogen phthalate, the properties of the resulting product being b. p. 121—122°/17 mm., α_D $-13{\cdot}44°$ in a 10 cm. tube.

The menthyl bromide obtained by Celikov (*loc. cit.*) has also been investigated further. It has b. p. 98—99°/14 mm., D_4^{20} 1·1504, α_D $-5{\cdot}20°$ in a 10 cm. tube. When boiled in ethereal solution with sodium, it yields menthane and menthene and crystalline and liquid dimenthyls, both lævo-rotatory.

The menthyl bromide prepared by the same method from menthyl hydrogen phthalate has b. p. 106—107°/20 mm., D_4^0 1·1749, D_4^{20} 1·1557, α_D $-23{\cdot}35°$ in a 10 cm. tube. T. H. P.

Menthylphenols. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1156—1171).—The author showed previously (A., 1915, i, 420) that phenyl menthyl ether is converted by heating with hydrochloric acid at 170° into a mixture of isomeric menthyl-

phenols, and similar mixtures are obtained when the constant or the crude menthyl chloride is heated with phenol. It is now shown that all these mixtures yield urethanes, m. p. 141° and 136° respectively, and also a small quantity of a fraction, m. p. 171—174°; the relative proportions of the different isomerides formed are similar in the various cases.

When crystalline menthylphenol is heated in a sealed tube with hydrochloric acid, part of it decomposes with formation of phenol and optically inactive menthyl chloride, the undecomposed part undergoing isomerisation into a mixture of crystalline and liquid menthylphenols.

As regards the position of the hydroxyphenyl group in the menthylphenols, the optical inactivity of these is explained by the assumption for them of the structure:

$$CHMe{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C(C_6H_4\cdot OH)\cdot CHMe_2.$$

Six isomerides of this formula are possible, all having symmetrical molecules. Such tertiary structure for the menthylphenols is confirmed by investigation of the menthyl chloride obtained when menthylphenols are heated with hydrochloric acid. This menthyl chloride is inactive, and, when boiled with alcoholic potash, is transformed into inactive menthene, such transformation being considerably more rapid than that of the unstable secondary menthyl chlorides contained in crude menthyl chloride. Further, the menthyl chloride in question gives instantaneously a copious precipitate with alcoholic silver nitrate solution. All these properties indicate the tertiary nature of the chlorine atom, which may be regarded as occupying the same position as the hydroxyphenol group in the menthylphenols.

The tertiary position of the hydroxyphenyl group in these menthylphenols is confirmed by comparison of the latter with those obtained on boiling menthene hydrochloride with phenol; the urethanes, m. p. 141° and 136°, but not that, m. p. 171—174°, are obtained in this case. When menthene is boiled with phenol in the presence of a small proportion of menthyl chloride, the isomeric menthylphenols formed consist principally of the one giving the urethane, m. p. 141°; other urethanes, m. p. 115—116° and m. p. 136°, are also obtained. In this reaction the menthyl chloride reacts with the phenol, liberating hydrochloric acid, which exerts a catalytic effect on the reaction. *Menthylphenyl phenyl ether*, $C_{10}H_9\cdot C_6H_4\cdot OPh$, prepared by heating the potassium derivative of menthylphenol with iodine and finely-divided copper (compare Ullmann and Sponagel, A., 1905, i, 644; 1907, i, 38), is a viscous, odourless, optically inactive oil, b. p. 223—225°/10 mm., D_4^{20} 1·0224. When this ether is heated with magnesium methyl iodide and the product of the reaction decomposed with ice, the resultant products are menthylphenol, phenol, and a menthyltoluene, which gives telephthalic acid on oxidation with dilute nitric acid in a sealed tube. The methyl group of the toluene residue, and consequently the hydroxyl group of the crystalline menthylphenol, thus occupies the para-position to the menthyl residue. T. H. P.

Phenyl *cyclo*Hexyl Ether and its Isomeration to *cyclo*Hexylphenol. N. I. KURSANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1172—1174. Compare A., 1915, i, 420).—*Phenyl* cyclo*hexyl ether*, $C_6H_{11}\cdot OPh$, prepared from *cyclo*hexanol by Ullmann and Sponagel's method (A., 1905, i, 644), is a viscous liquid, b. p. 140°/21·5 mm., 260—262°/759 mm., D_4^0 1·0241, D_4^{20} 1·0077. When heated with fuming hydrochloric acid in a sealed tube at 180° it is partly decomposed into *cyclo*hexyl chloride and phenol, $C_6H_{11}\cdot OPh + HCl = C_6H_{11}Cl + Ph\cdot OH$, and partly isomerised into *p*-*cyclo*hexylphenol (compare A., 1902, i, 20). T. H. P.

Nomenclature of the Fenchenes. New Method of Preparing β-Fenchene. GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. fennicae*, 1915, [*A*], **7**, No. 14, 1—8; from *Chem. Zentr.*, 1917, i, 407).—The nomenclature α- and β-fenchene is proposed, the former being applied to the substance which yields the hydroxyfenchenic acid and the fenchocamphorone of higher m. p. Wallach's *dl*-fenchene is therefore *l*-α-fenchene, his *d*-α-fenchene is *d*-β-fenchene, and the racemic form of the latter is *dl*-β-fenchene.

β-Fenchene, almost free from the α-variety, but mixed with other isomeric hydrocarbons, can be obtained by heating fenchyl alcohol with potassium or sodium hydrogen sulphate or from active fenchyl alcohol, b. p. 196—198°, by distilling a mixture of the finely powdered alcohol with three times its weight of powdered melted potassium hydrogen sulphate in a stream of carbon dioxide at 170—180°. After repeated fractionation over sodium, the hydrocarbon has b. p. 151—153°, D 0·8660, $[\alpha]_D$ +10·7°. On oxidation, it yields hydroxyfenchenic acid, m. p. 138—139°, and hence consists of pure β-fenchene. Inactive, racemic fenchyl alcohol is obtained through fenchyl hydrogen phthalate, m. p. 165—167°, and has b. p. 198°/757 mm., m. p. 33—35°. When distilled with sodium hydrogen sulphate, it yields a mixture of β-fenchene and other hydrocarbons. Repeated fractionation yields a portion, b. p. 151—153°, D_4^{17} 0·8598, n_D^{17} 1·46620; n_α^{17} 1·46379, n_γ 1·47924, MR_D 43·89, $MR_y - MR_\alpha$ 1·24. Oxidation with alkaline permanganate converts it into *r*-hydroxy-β-fenchenic acid, $C_{10}H_{16}O_3$, m. p. 125—126°, which forms a sparingly soluble sodium salt. Further oxidation with acid permanganate transforms the acid into *r*-β-fenchocamphorone, b. p. 196—197°, m. p. 64—66° (semicarbazone, m. p. 195—196°). When treated with alkaline permanganate at 50—60°, the ketone yields a dibasic *acid*, $C_9H_{14}O_4$, m. p. 144—145°, which is isomeric with *apo*camphoric acid. Since it does not yield an anhydride with acetyl chloride, it is probably a *trans*-acid. The substance is still under investigation.
H. W.

The Turpentine obtained during the Sulphate-Cellulose Process. O. M. HALSE and HERMAN DEDICHEN (*Ber.*, 1917, **50**, 623—630).—During the treatment of wood for cellulose by the sulphate process, varying quantities of a turpentine-like oil, mixed with evil-smelling sulphur compounds, are collected in the condensed steam. The amount varies, for example, from 1 kilo. in the

case of the larch to 10 kilos. with the pine per ton of cellulose. Such an oil has now been submitted to a systematic examination of the usual type, after removing the sulphur compounds by means of alcoholic mercuric chloride. Like ordinary turpentine-oils, the main fraction consists of α-pinene, and it is interesting that this terpene should withstand the sulphate treatment. In the sulphite-cellulose process it is entirely changed into *p*-cymene. A small amount of β-pinene is also present, but in a dextro-rotatory modification, and probably dipentene as well. α-Pinene was identified by conversion into pinonic acid and bornyl chloride, β-pinene by oxidation to nopic acid. J. C. W.

Polymerisation of Isoprene, Divinyl, and Dimethylerythrene to Caoutchouc or its Homologues. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1071—1114).—The author has investigated the different caoutchoucs obtained by polymerisation from (1) mixtures of isoprene with amylenes, (2) isoprene, (3) mixtures of erythrene with butylenes, (4) erythrene, and (5) βγ-dimethylerythrene. The determination of the physical properties of different caoutchoucs and that of the two new constants (A., 1916, i, 54) renders it necessary to modify the views formerly held with respect to their constitution, and the author now considers that higher and lower caoutchouc-like polymerides of one and the same diolefine do not exist, but that the various isomeric caoutchoucs are polymerides of one and the same magnitude. Thus, the isomerism of "individual" caoutchoucs is determined solely by the positions of the ethylene linkings of the nucleus or by the positions of the methyl groups in the side-chains.

The four isoprene caoutchoucs described below are obtained under conditions of catalytic thermo-polymerisation which, when applied to erythrene, yield always one and the same caoutchouc. In erythrene caoutchouc, as in erythrene, there are no methyl groups, but the number of double linkings present is the same as in isoprene caoutchouc. Consequently, the isomerism of α-, β-, γ-, and δ-isoprene caoutchoucs is conditioned by differences in the positions of the methyl groups, that is, of the side-chains.

The same conclusion may be drawn from the existence of only one form of βγ-dimethylerythrene caoutchouc. The two methyl groups of βγ-dimethylerythrene are arranged symmetrically in the molecule, and thus, unlike the single methyl group of isoprene, cannot give rise to isomerides. The isomerism of normal γ-isoprene caoutchouc with normal ε-caoutchouc is, however, probably conditioned by the different positions occupied by their ethylene linkings, since the conditions in which these isomerides are formed are those in which the corresponding isomerides of erythrene caoutchouc are obtained.

Two abnormal isoprene–amylene caoutchoucs are described: (1) the α-form, obtained first by Matthews and Strange (Eng. Pat., 24790, 1911), and later, under the name of sodium–isoprene caoutchouc, by Harries; (2) the β-isomeride, here described for the first time and prepared in quantitative yield by the catalytic action of

barium peroxide or benzoyl peroxide on the α-form in toluene solution.

α-Isoprene–amylene caoutchouc forms a viscous, sticky mass which adheres firmly to wood, metal, glass, etc., and is easily drawn out into long threads; when exposed to the air it becomes covered with an oxidised layer, which is non-adhesive. When vulcanised, it yields a product which is not sticky or plastic, but is also devoid of the elastic properties of natural caoutchouc and may be easily torn like a rotten rag; its elastic point evidently lies above its temperature of decomposition. This caoutchouc has no industrial application, and when added to natural caoutchouc, even to the extent of only 1%, appreciably lowers the value. The molecule of α-isoprene–amylene caoutchouc probably contains the amylene as a saturated radicle, $\cdot CMe_2\cdot CHMe\cdot$, the proportion of bromine combined diminishing as that of the amylene mixed with the isoprene increases. The structure may be represented thus:

$$\begin{array}{l} CH_2\cdot CMe{:}CH\cdot CH_2\cdot \ .\ .\ .\ .\ \cdot CMe_2\cdot CH_2 \\ | \hspace{18em} | \\ CH_2\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH{:}CMe\cdot CH_2 \end{array}.$$

That amylene is present in the molecule is supported by the gradual and direct alteration of the physical properties as the proportion of amylene used increases; for example, the liquid state is more and more nearly approached. Elementary analysis is insufficient to detect the presence of even considerable proportions of amylene. If, in the preparation of α-isoprene–amylene caoutchouc, the amylene is replaced by *iso*butylene, caoutchoucs with similar properties are obtained.

β-Isoprene–amylene caoutchouc forms a compact mass quite free from pastiness, and at about 100° assumes all the elastic properties of natural caoutchouc, its elasticity point being thus lower than that of the α-isomeride. In the air, β-isoprene–amylene caoutchouc is oxidised moderately rapidly to a very compact, solid, amorphous, oxygenated mass which gives a blow like a stone and is readily pounded to a fine powder; as the oxidation proceeds, the elasticity point and the fatal temperature gradually rise. Vulcanisation converts it into a product which at 80—90° exhibits all the properties of vulcanised natural caoutchouc.

α-Isoprene caoutchouc, prepared by the action of sodium on chemically pure isoprene at 60—75° for ten to forty hours, differs considerably from α-isoprene–amylene caoutchouc, which is obtained from isoprene containing amylene, in particular from the isoprene prepared by the catalytic removal of two molecules of hydrogen chloride from dichloro*iso*pentane at a low pressure. α-Isoprene caoutchouc represents a colourless, non-gluey, non-fluid, insoluble mass, transparent as glass, which can be rolled hot or easily broken, but not drawn into threads; it swells up slowly and slightly in various media, but does not dissolve even in traces. Its elasticity is low, and the noise of its impact resembles that of a solid body. It is an abnormal caoutchouc, its elasticity point lying above 110° and its fatal temperature somewhat below 0°; at about 110° it assumes all the elastic properties of natural caoutchouc. It is

vulcanised by sulphur or nitro-compounds, although more slowly than caoutchoucs of the normal series, and it is applicable in practice only for certain special purposes.

β-Isoprene caoutchouc, obtained in quantitative yield by the action of a mixture of sodium with barium (or benzoyl) peroxide on pure isoprene at 60—70°, has usually a pale cinnamon colour and is transparent in thin layers; it flakes, but has no stickiness or fluidity, and may be rolled comparatively easily even at 60°. It is an abnormal caoutchouc, its elasticity point being about 80—90°, which is somewhat lower than that of the α-isomeride, and its fatal temperature about −10°.

γ-Isoprene caoutchouc, prepared in small yield (40%) by the action of barium or benzoyl peroxide or an alkaline sulphide or polysulphide at 45—50° for two to four months, is an almost colourless, brittle, amorphous substance, transparent as glass, which cannot be drawn into threads, but is possessed of considerable elasticity and spring; after deformation, it resumes its original form and dimensions almost instantaneously. It is a normal caoutchouc, its elasticity point and fatal temperature being almost identical with those of natural caoutchouc.

δ-Isoprene caoutchouc, prepared from β-myrcene (compare Ostromisslenski and Koschelev, A., 1916, i, 274), is of the normal series.

ϵ-Isoprene caoutchouc is the name proposed by the author for the caoutchouc obtained in quantitative yield by gently heating isoprene with sodium in an atmosphere of carbon dioxide. It is formed also by the action of the ultra-violet light of the quartz lamp on isoprene in presence of sodium and carbon dioxide. It is a normal isoprene caoutchouc and quite insoluble. This form appears to be a physical isomeride of the normal γ-isoprene caoutchouc, the elasticity points and the fatal temperatures being apparently the same for the two. Towards a mixture of sodium and carbon disulphide isoprene caoutchouc is quite passive, both at the ordinary temperature and on heating.

Recovered caoutchouc is always abnormal, its fatal temperature and elasticity point being relatively high; only above 120° does it regain the elastic properties of ordinary caoutchouc. The process of recovery is evidently accompanied by rearrangement in the nucleus.

α-Erythrene caoutchouc is obtained by heating erythrene alone or with sodium (0·3—0·5%), barium peroxide, sodium and barium peroxide, or first one of these and then the other. When, however, the erythrene is heated in presence of sodium and in an atmosphere of carbon dioxide, it is converted into an insoluble ϵ-caoutchouc analogous to the normal insoluble ϵ-isoprene caoutchouc obtained under similar conditions from isoprene. The isomerism appears to be of a chemical character and conditioned only by the different positions of the ethylene linkings in the molecule. A third isomeride (α') is often formed in small proportion, together with the α-variety, when erythrene is heated with sodium in absence of carbon dioxide. This differs from α-erythrene caoutchouc only in its insolubility, and is a highly elastic, colourless substance, transparent as glass, which

swells in light petroleum, turpentine, etc., and is readily vulcanised under the ordinary conditions given for the vulcanisation of synthetic caoutchoucs (A., 1916, i, 55).

α-Erythrene caoutchouc is a colourless, transparent, elastic, highly resilient substance, which does not stick, and is readily rolled in the hot, but if rolled in the cold requires a slight admixture of a liquid of high boiling point, since otherwise it crumbles between the rolls like factis; after deformation, if not too prolonged, it recovers its form and dimensions almost instantly. This caoutchouc belongs to the normal series, its elasticity point and fatal temperature being somewhat lower than those of Para caoutchouc; thus, at normal temperatures it is more elastic than natural caoutchouc, and it remains elastic when Para caoutchouc reaches its elasticity point. It is vulcanised more rapidly and easily than the natural rubber under ordinary conditions or by means of benzoyl peroxide, nitro-compounds, chlorine, etc. The vulcanised product is highly elastic and resilient and its residual elongation negligible; it is more resistant to deformation than vulcanised natural caoutchouc, but its resistance to shearing is slight. If, before vulcanisation, the caoutchouc is caused to swell by means of albumin or some other substance with colloidal properties, the resultant product corresponds in properties with vulcanised natural caoutchouc.

α-Erythrene–butylene caoutchouc, prepared by the action of sodium on erythrene containing butylenes, closely resembles α-isoprene–amylene caoutchouc.

β-Erythrene–butylene caoutchouc, prepared by heating a toluene solution of the α-isomeride with barium peroxide (0·5—5%) at 60—75° for one to seven days, is not sticky, exhibits great compactness, is somewhat resistant to shearing, cannot be drawn into threads, and is moderately easily rolled in the cold. It belongs to the normal series and is readily vulcanised to a product showing all the properties of vulcanised natural caoutchouc; it dissolves in benzene, light petroleum, turpentine, etc. The isomerisation of the α- to the β-isomeride occurs only if the former contains comparatively little butylenes, erythrene containing 10—15% of the latter being utilisable.

All the caoutchoucs which have been obtained from βγ-dimethylerythrene (compare Couturier, A., 1893, i, 244; Kondakov, A., 1901, i, 625; Harries, A., 1911, i, 798) have been investigated, and are found to be identical; they usually contain varying proportions of the dimeride and of foreign liquids, which lower the elasticity point and the fatal temperature. The form obtained by the action of sunlight on the monomeride (α′) does, indeed, differ from that resulting from the thermopolymerisation of the βγ-dimethylerythrene (α) by its solubility in various media, but this difference is doubtless conditioned by differences in the physical state, the two being merely colloidal modifications of one and the same hydrocarbon. A number of different catalysts were employed, but in all cases the α-form was obtained in the hot and mostly the α′-form at temperatures up to 20—30°. Further, polymerisation of βγ-dimethylerythrene in presence of foreign ethylenes yields always the

ordinary α- or α'-modification, mixed or "combined" forms not being obtained in this case.

The α-form of $\beta\gamma$-dimethylerythrene caoutchouc, obtained at any temperature from 40° to 170°, and especially rapidly in the presence of a small proportion (1%) of piperidine piperidyldithiocarbamate, belongs to the abnormal series, its elasticity point being 125—130° and its fatal temperature −5°. When vulcanised it acquires all the elastic properties of natural caoutchouc at 100°. T. H. P.

Preparation of Substances Equivalent to Ebonite, Celluloid, or Guttapercha. Synthesis of Vulcanised Caoutchouc. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1114—1131).—When treated with free chlorine, either natural or synthetic caoutchouc is converted into a substance which exhibits the properties of ebonite, in some cases to an enhanced degree. In its stability towards alkali or high temperatures it is the equal of ebonite, and, unlike the latter, it is very stable towards acids. Thus, the product obtained by the action of chlorine on synthetic normal erythrene caoutchouc is not changed by the prolonged action of nitric acid (D 1·35), by boiling fuming hydrochloric acid (D 1·19), by boiling chromic acid, or by concentrated sulphuric acid. It may be worked and polished like the best ebonite obtained from caoutchouc and sulphur, and is equally plastic. Its specific gravity is almost equal to that of ebonite and it is a better electrical insulator, its conductivity approximating to that of the best types of glass and baekelite. Ordinarily it is black, but if prepared under certain special conditions it may be obtained almost white or even colourless and transparent, and it is easily coloured. An ebonite-like substance may also be obtained by heating caoutchouc chloride or bromide (A., 1916, i, 278) in an iron mould out of contact with air at the ordinary temperature employed in vulcanising caoutchouc, but the product yielded in this way is always more or less porous.

Caouprene chloride, readily obtainable either from ethyl alcohol and sodium chloride through mono- or di-chloroethane (this vol., i, 405), or from carbon, lime, and hydrochloric acid through calcium carbide, may be easily converted into a plastic mass equivalent in its properties to celluloid, guttapercha, or the best ebonite. When treated with a very small proportion of naphthalene or copper oleate, the chloride yields a highly coherent ebonite; with camphor, paraffin-wax, or hexachloroethane a product corresponding with celluloid is obtained, whilst with oils, such as paraffin oil, esters, tri-, tetra-, or penta-chloroethane or with a large excess of naphthalene, etc., a substance with all the properties of natural guttapercha is formed. This synthetic ebonite exhibits the mechanical properties of ordinary ebonite, and is furthermore non-inflammable and of high stability towards acids or an atmosphere of moist chlorine.

Analogous products are obtainable in a similar manner from the higher chloride of caoutchouc, $C_{40}H_{48}Cl_{32}$, or the homologous chlorocaouprene chloride.

Experimental details are given. T. H. P.

Synthesis of the Symmetrical Chloride and of the Higher Chloride of Erythrene Caoutchouc. New Chlorides of Natural Isoprene and Erythrene Caoutchoucs. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **46**, 1132—1151).—It has been already shown that polymerised vinyl bromide represents the symmetrical bromide of erythrene caoutchouc (A., 1916, i, 273), and the natural supposition that caouprene chloride is the corresponding symmetrical chloride is now justified experimentally.

Baumann (A., 1872, 890) described caouprene chloride as a viscous, plastic, insoluble mass, but these properties are caused by admixtures of extraneous liquids, such as the higher chloro-derivatives of ethane, esters of the fatty acids, etc., the chemically pure chloride being a snow-white, amorphous mass readily reducible to a fine powder. Caouprene chloride is rapidly formed by the action of the light from a mercury quartz lamp on liquid vinyl chloride, and exists in a soluble α-modification, which swells in various media to a more or less mobile layer, and in a more stable, insoluble γ-form; the former is completely converted into the latter by prolonged heating at 30—40° or by the action of the light from a mercury lamp. The relation between the α- and γ-caouprene chlorides is undoubtedly analogous to that between the α- and α′-forms of βγ-dimethylerythrene caoutchouc (this vol., i, 402). The asymmetric chlorides of erythrene caoutchouc, and natural caoutchouc also exist in two modifications, namely, a soluble α- and an insoluble γ-modification. The molecular weight of α-caouprene chloride, measured cryoscopically in ethylene bromide solution, is 1021, which corresponds with the molecule $(CH_2{\cdot}CHCl)_{16} = 999$; this result is in agreement with that obtained for caouprene bromide.

When heated with one of a number of different compounds, α- and γ-caouprene chlorides give ebonite-like substances which are identical with those obtained under analogous conditions from the asymmetric chloride of erythrene caoutchouc, and in their physical and mechanical properties closely resemble the ebonites obtained from the chloride of natural Para caoutchouc.

Like the bromide, caouprene chloride is a unicyclic halogenide, the ring containing sixteen $-CHCl{\cdot}CH_2-$ groups. The absence of double linkings is shown by its behaviour towards various reagents, such as permanganate, tetranitromethane, etc., and especially by its stability towards oxidising agents, like chromic acid and concentrated nitric acid (D 1·35), by its passivity towards halogen hydracids, including boiling hydrochloric acid, and towards concentrated sulphuric acid, and by the ability of the halogen present to react.

Unlike all natural and synthetic caoutchoucs and all their known halogenated derivatives, which are absolutely insoluble in acetone, α-caouprene chloride dissolves readily in this solvent. Gradual addition of a solution of the calculated amount of chlorine in carbon tetrachloride to a solution of erythrene caoutchouc in the same solvent yields an asymmetric chloride of erythrene caoutchouc, $C_{32}H_{48}Cl_{16}$, isomeric with caouprene chloride, from which it

differs only in the positions of the halogen atoms; this chloride also dissolves readily in acetone. Under the same conditions, natural caoutchouc gives a chloride of normal composition, $C_{32}H_{40}Me_8Cl_{16}$, also readily soluble in acetone. Like caouprene chloride, each of these chlorides exists in α- and γ-modifications. Owing to the solubility of the chlorides in acetone, they may be freed from admixtures of free caoutchouc and of colloidal higher chloride, and thus obtained in a chemically pure condition.

The polymeride of dichloroethylene yields a peculiar ebonite and is termed, by analogy, chlorocaouprene chloride. It is isomeric with the higher chloride of erythrene caoutchouc, obtained by the action of chlorine on a solution of the free caoutchouc, the isomerism depending on the position of the halogen. Under the influence of the active light of a quartz mercury lamp, *as.*-dichloroethylene polymerises almost instantly.

Caouprene chloride has been prepared from ethyl alcohol and chlorine by the following reactions: (1) $EtOH = C_2H_4 + H_2O$, (2) $C_2H_4 + Cl_2 = C_2H_4Cl_2$, (3) $C_2H_4Cl_2 + NaOH = NaCl + H_2O + CH_2{:}CHCl$, and (4) $16CH_2{:}CHCl = (CH_2{:}CHCl)_{16}$. Owing to the "poisoning" of the alumina used as catalyst in the catalytic dehydration of alcohol, the yield of ethylene obtained gradually falls. It is found that this alumina may be regenerated by cautious ignition in a current of air and subsequent treatment with superheated steam. The yield of ebonite obtained amounts to at least 60 to 75 parts per 100 parts of absolute alcohol, and this is probably capable of considerable increase by varying the experimental conditions employed. Pure vinyl chloride has b. p. $-12°$, and not $-18°$ as stated in the literature.

The asymmetric chloride of erythrene caoutchouc, $C_{32}H_{48}Cl_{16}$ (vide supra), is a snow-white, amorphous mass, which is readily powdered and becomes electrified when sieved through silk; it cannot be distinguished from caouprene chloride. It behaves towards permanganate like a saturated compound, remains colourless when treated with tetranitromethane, reacts with phenol, losing hydrogen chloride, and is passive towards nitric acid (D 1·35), concentrated sulphuric acid, boiling fuming hydrochloric acid (D 1·19), and boiling chromic acid. Under similar conditions, this chloride and caouprene chloride yield one and the same ebonite or one and the same plastic mass resembling celluloid or gutta-percha; the two substances behave similarly towards camphor, naphthalene, copper oleate, etc., and are soluble in the same solvents.

The chloride of natural Para caoutchouc cannot be distinguished from that of synthetic normal γ-isoprene caoutchouc, although they undoubtedly differ in the positions of the methyl groups in the nucleus. They are almost white, amorphous substances, which become electrified when rubbed, and, when pure, are easily powdered. Chemically and physically they behave like homologues of the chlorides of erythrene caoutchouc.

When treated in light petroleum (b. p. up to 80°) solution with

a current of anhydrous chloride at 0°, α-erythrene caoutchouc yields a higher chloride, $C_{32}H_{32}Cl_{32}$, which is white, amorphous, and opaque, and may be readily crushed. T. H. P.

Catalytic Acceleration of the Vulcanising Process. S. J. Peachey (*J. Soc. Chem. Ind.*, 1917, **36**, 424—429).—An account is given of the earlier history of vulcanisation and of the use of mineral accelerators. The first powerful organic accelerator to be used appears to be piperidine (Bayer & Co., D.R.-P., 265221, 1912); subsequently the use of all organic bases possessing a dissociation constant greater than 1×10^{-8} has been patented by the same firm (D.R.-P., 280198, 1914).

The author has found that the nitroso-derivatives of certain bases, such as dimethylaniline, methylaniline, and diphenylamine, are capable of acting as powerful accelerators of the vulcanising process (Brit. Pat., 4263, 1914). Generally speaking, the addition of 0·3 to 0·5% of nitroso-base to any mixing of good quality is sufficient to reduce the time of vulcanisation to from one-quarter to one-third of that normally required. In the case of red mixings containing antimony sulphide as the vulcanising agent and no added sulphur, the accelerator fails to develop its full effect. In such cases it becomes necessary to introduce a certain amount of sulphur and to employ the sulphide mainly as a pigment. The presence of litharge in any quantity tends to diminish the effectiveness of the organic accelerator whilst, on the other hand, magnesia in small amounts very considerably augments the accelerating power of the nitroso-base. The maximum accelerating power of *p*-nitrosodimethylaniline is only fully manifested when new rubber is used.

The action of organic accelerators appears to be entirely catalytic in its nature.

It may be noted that whilst the nitroso-derivatives of such bases as methylaniline, ethylaniline, diphenylamine, and others are powerful accelerators, the isomeric nitrosoamines have not a similar effect.

The catalytic action of the nitroso-bases appears to depend on the presence of the nitroso-group, and not on their basic nature; it is also shown by certain nitroso-compounds, which are quite destitute of basic properties, for example, nitrosophenol and nitrosonaphthol.

It has further been found that the condensation products formed by the action of amines on aldehydes, for example, benzylidene-ethylamine, benzylideneaniline, and hydrobenzamide (Brit. Pat., 7370, 1914), have a marked effect in accelerating the vulcanisation of rubber, but they are considerably less effective than the nitroso-compounds.

It is interesting to note that certain substances, such as phenylhydrazine, have an anti-catalytic action on the vulcanisation of rubber. H. W.

The Constitution of Amygdalin. ARMINIUS BAU (*Biochem. Zeitsch.*, 1917, **80**, 159—162).—*Saccharomycodes Ludwigii* (Hansen) contains amygdalase as well as yeast emulsin, but no maltase. The facts confirm the views expressed by Auld, Caldwell, and Courtauld that the disaccharide of amygdalin, $C_{12}H_{22}O_{11}$, is not maltose, although it undergoes scission into two molecules of dextrose. S. B. S.

Chemical Constitution of Chitin. S. MORGULIS (*Science*, 1916, **44**, 866—867; from *Physiol. Abstr.*, 1917, **2**, 103).—In the hydrolysis of chitin (from lobsters) by sulphuric acid very little volatile acid is formed at first, although all the dextrose molecules may have been split off. A large amount of volatile acid is formed when the sugar itself is attacked by the acid. In addition to acetic, some formic acid is formed (up to 2%) and probably also other volatile acids. The maximum yield of sugar is 81%. The amino-group is readily eliminated from the glucosamine as ammonium sulphate. The amino-nitrogen represents only seven-eighths of the total nitrogen, the more resistant remaining nitrogen fraction being obtained by digestion with concentrated sulphuric acid; the relation between the two kinds of nitrogen is remarkably constant. These results do not confirm the prevalent idea that chitin is a polymerised acetylglucosamine. The molecule apparently consists of two parts, one containing all the dextrose and all the amino-groups, the other being a stable nitrogen compound not yielding dextrose. The acetic acid is not a primary fission product, but a secondary product of the hydrolysis, and the same is true of monoacetylglucosamine or monoacetyldiglucosamine. G. B.

Solanine. A. HEIDUSCHKA and H. SIEGER (*Arch. Pharm.*, 1917, **255**, 18—44).—An examination of solanine obtained from potato shoots.

On account of the tendency of solanine to decomposition and to sublimation, the m. p. of the substance is rather indefinite; a more valuable characteristic is the optical activity in 2% hydrochloric acid, $[\alpha]_D^{20}$ $-42{\cdot}16°$.

The composition of the pure substance obtained in the present investigation was different from that given by earlier workers, and agreed best with a formula $C_{52}H_{91}O_{18}N$. Contrary to previous statements (Zwenger and Kind, *Annalen*, 1859, **109**, 244), the hydrochloride ($C_{52}H_{91}O_{18}N,HCl$) was obtainable in a crystalline condition, m. p. 212° (decomp.), after sintering at 177°, but no oxalate could be isolated.

Hydrolysis of solanine is best effected with 2% hydrochloric acid solution; the resulting solanidine, m. p. 207°, judged by its composition and molecular weight in phenol, possesses the formula $C_{34}H_{57}O_2N$. The hydrolytic fission of solanine is not complete, but, by allowing for the unaltered solanine, and measuring the extent to which the resulting sugars affect Fehling's solution, it is calculated that each molecule of solanine gives one molecule each of solanidine, dextrose, galactose, and rhamnose.

Heating with ethyl iodide in alcoholic solution failed to effect the introduction of the ethyl radicle, and attempts at acetylation failed to give any definite product (compare Hilger, A., 1879, 541). The dehydration of solanidine by concentrated hydrochloric acid or other agents yielded not only solanicine, $C_{34}H_{55}ON$, but also a base intermediate between this and solanidine probably derived from solanidine by the elimination of a semi-molecular proportion of water.

Solanine was also found to form an additive *compound* with phytosterol, and also, when heated, to evolve vapours which redden a pine shaving.

An examination of solanine from the *Palo Natri* of Chile showed this substance to be identical with the product from potatoes.

D. F. T.

Bixin. A. HEIDUSCHKA and A. PANZER (*Ber.*, 1917, **50**, 546—554).—The empirical formulæ assigned to bixin by van Hasselt, Heiduschka, and Riffart, and Herzig and Faltis seem to depend on the method by which the pigment is purified. Analyses based on various methods of isolation and crystallisation are now discussed, but it appears that most dependence is to be placed on a specimen which has been purified by acetone in the usual way and then crystallised from ethyl acetate. The analysis and methoxyl and molecular-weight determinations of such a product agree with the formula $C_{25}H_{30}O_4$, which was obtained by Pregl on behalf of Herzig and Faltis (A., 1915, i, 572). J. C. W.

Action of Furfuraldehyde on Cinnamylidenemethyl Methyl Ketone. M. GIUA (*Gazzetta*, 1917, **47**, i, 86—89).—By the condensation of furfuraldehyde (1 mol.) with cinnamylidenemethyl methyl ketone (1 mol.) in presence of sodium hydroxide, Bauer and Dieterle (A., 1911, i, 921) obtained β-styryl β′-furyldivinyl ketone. The author finds that this condensation yields also *difurfurylidenetricinnamylideneacetone*,

$$CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CH\left(CH{<}{\begin{matrix}C_4H_3O\\CH_2\cdot CO\cdot CH{:}CH\cdot CH{:}CHPh\end{matrix}}\right)_2,$$

which forms golden-yellow crystals, m. p. 215—216°, gives a brick-red coloration with concentrated sulphuric acid, and may also be obtained by polymerisation of β-styryl β′-furyldivinyl ketone in benzene solution in sunlight; indications of the existence of a second stereoisomeride were obtained (compare v. Kostanecki and Rossbach, A., 1896, i, 551; v. Kostanecki and Podrajansky, A., 1896, i, 689). T. H. P.

Bromine Substitution Products of Chromones [Benzopyrones]. H. SIMONIS and L HEROVICI (*Ber.*, 1917, **50**, 646—652).—The bromination of 2:3-dimethylchromone is described (compare A., 1913, i, 890). In the cold, this compound merely absorbs bromine at the ethylene linking, but the halogen atoms are given up again when the product is dried. Under more strenuous conditions, the methyl groups are attacked, but the benzene nucleus is

only affected in extreme cases, which is proved by the fact that the simpler bromo-derivatives yield unsubstituted salicylic acid on hydrolysis.

With bromine in boiling benzene the products are *ω-bromo-2:3-dimethyl-γ-benzopyrone*, $C_6H_4<\overset{CO}{\underset{O}{}}>C_2Me\cdot CH_2Br$, m. p. 171—172°, and *ωω-dibromo-2:3-dimethylbenzopyrone*, prisms, m. p. 193°, which is the less soluble in ether of the two. Except that the bromine atoms are in the side-chains, no more can be said as yet with regard to their positions relative to the pyrone ring. The monobromide may be hydrolysed by alcoholic silver nitrate to an oily *hydroxy*-compound. Bromination in carbon disulphide solution under pressure at 140° gives rise to the same products unless at least four molecular proportions of bromine and a little iodine are used, when a *tetrabromo*-compound, rhombic plates, m. p. 215°, and two less soluble *tribromo*-derivatives, prisms, m. p. 168°, and stellate groups of needles, m. p. 185°, are formed. There are indications of the presence of the $-CHBr_2$ group and of bromine in the benzene nucleus in these compounds. J. C. W.

Scopoline Bromide. ERNST SCHMIDT (*Arch. Pharm.*, 1917, **255**, 72—75. Compare A., 1916, i, 285, 419).—For a final decision as to the constitution of scopoline it is necessary to ascertain the nature of the oxygen atom adjacent to the hydroxyl radicle. From the chemical inactivity of this oxygen atom it appears probable that an ether grouping is present, but in order to avoid the possibility that the inertness of this oxygen atom may be due to the proximity of the hydroxyl group, the author has prepared *scopoline bromide*, $C_{18}H_{12}ONBr$ (*hydrobromide*, prisms, m. p. 226—227° decomp.; *aurichloride*, pale red cubes, m. p. 211° decomp.; *platinichloride*, brownish-red prisms or needles, m. p. 221—222°), by the action of phosphorus pentabromide on scopoline hydrobromide.

In this compound the hydroxyl group of scopoline has been replaced by a bromine atom, and the chemical behaviour of the remaining oxygen atom is to be examined further. D. F. T.

Alkaloids of Ipecacuanha Root, Uragoga Ipecacuanha. III. OSKAR KELLER (*Arch. Pharm.*, 1917, **255**, 75—80. Compare A., 1914, i, 428; 1911, i, 1014).—The paper consists of a commentary on the results of the author in comparison with those of Hesse (A., 1914, i, 722), Carr and Pyman (T., 1914, **105**, 1591), Hermanns (*Diss.*, Freiburg, 1915), Karrer (A., 1916, i, 833), and Paul and Cownley (A., 1894, i, 155). D. F. T.

The Alkaloids of Ipecacuanha. II. P. KARRER (*Ber.*, 1917, **50**, 582—586. Compare A., 1916, i, 833).—Karrer finds that his oxidation product, "dehydroemetine," is identical with Carr and Pyman's "rubremetine" [as Pyman has also suggested in the meantime; see T., 1917, **111**, 423].

Carr and Pyman experienced a difficulty in the reduction of dehydroemetine (rubremetine), but it is now found that the iodide

is readily reduced to an isomeride of emetine by the gradual addition of zinc dust to a boiling solution in a mixture of dilute acetic and sulphuric acids. iso*Emetine* is an amorphous substance, m. p. 50—55°, which couples with diazotised sulphanilic acid even in neutral solution, giving a product which becomes deep bluish-violet with acids and is thus distinguished from emetine. The *hydrobromide* and *hydriodide*, B,2HX, and the *dimethiodide* of N-*methyl*iso*emetine*, $C_{29}H_{39}O_4N_2Me,2MeI$, m. p. 185—195°, have been prepared. J. C. W.

Alkaloids of Ipecacuanha. II. FRANK LEE PYMAN (T., 1917, **111**, 419—446. Compare T., 1914, **105**, 1591).—In extension of the earlier work, two new alkaloids of ipecacuanha have been examined and *N*-methylemetine investigated more fully.

The non-phenolic, ether-soluble alkaloids are converted into the hydrobromides and the aqueous mother liquor left after crystallising the emetine salt is so treated that the hydrogen oxalates of the minor bases are isolated. The mixture is basified and the alkaloids separated by fractional extraction with acids from the chloroform solution. The more basic alkaloid, amounting to 0·015 to 0·033% of ipecacuanha, is shown to be identical with the O-*methyl ether* of *psychotrine*. This yields emetine and *iso*emetine on reduction (and another base, designated "C"), just as psychotrine yields cephaeline and *iso*cephaeline. Conversely, when emetine is oxidised with two atomic proportions of iodine, it yields methylpsychotrine, and both these further give rubremetine on oxidation with more iodine or bromine. Methylpsychotrine forms an *N*-benzoyl derivative, and therefore these bases are secondary.

The less basic alkaloid amounts to about 0·002—0·006% of ipecacuanha. It is designated *emetamine* and probably contains a –C⁚C– and a –C⁚N– linking.

N-Methylemetine salts are described, and its degradation to a methine, according to the scheme:

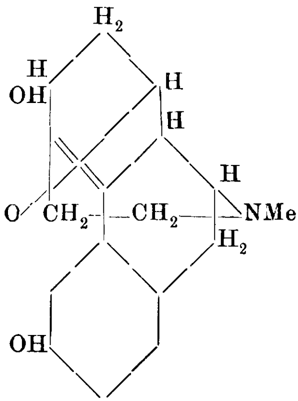
$$\underset{\textit{N}\text{-Methyl-emetine.}}{C_{30}H_{42}O_4N_2} \longrightarrow \underset{\textit{N}\text{-Methylemetine dimethohydroxide.}}{C_{32}H_{48}O_4N_2(OH)_2} \longrightarrow \underset{\textit{N}\text{-Methylemetine-methine.}}{C_{32}H_{46}O_4N_2}$$

For the detailed account of the many new salts and derivatives the original must be consulted. J. C. W.

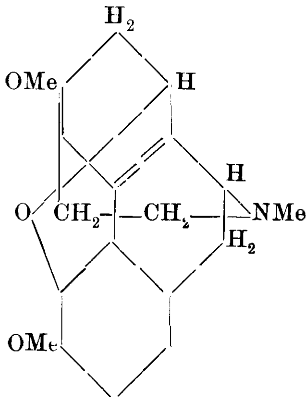
Cephaeline Butyl Ether and Salts thereof. J. W. MEADER (Brit. Pat., 104652; addition to Brit. Pat., 11717; from *J. Soc. Chem. Ind.*, 1917, **36**, 520).—*Cephaeline butyl ether* [as distinguished from the *iso*butyl ether claimed in the principal patent (this vol., i, 91)] is prepared by the action of an alkali metal and a butyl haloid on cephaeline. The details of the preparation and the properties of the product are the same as for the *iso*butyl ether. H. W.

Preparation of Cephaeline Allyl Ether. ELI LILLY & Co. (U.S. Pat., 1209575; from *J. Soc. Chem. Ind.*, 1917, **36**, 520).—*Cephaeline allyl ether*, $C_{28}H_{37}O_3N_2{\cdot}O{\cdot}C_3H_5$, is prepared by treating cephaeline with sodium ethoxide and allyl bromide. H. W.

Constitution of Morphine. FRANZ FALTIS (*Arch. Pharm.*, 1917, **255**, 85—112).—A critical review of most of the work on morphine and its related bases accomplished by Vongerichten, Knorr, Freund, and von Braun during the last ten years or so. It is shown that the conflicting results can be explained on the basis of the annexed formulæ for morphine and thebaine, in which the oxide ring is different from that in Knorr's formula and is under considerable tension.



Morphine.



Thebaine.

J. C. W.

An Anomaly in the Solubility of Sparteine. AMAND VALEUR (*Compt. rend.*, 1917, **164**, 818—820).—A saturated aqueous solution of sparteine becomes turbid with a very slight rise in temperature, but if the solution is diluted, a greater rise in temperature is necessary to produce turbidity. This phenomenon is exhibited by all solutions down to a dilution of 0·14 gram per 100 c.c. In the presence of sodium carbonate, much more dilute solutions become turbid. The values of the temperature at which turbidity occurs for various dilutions of sparteine in the presence of 5% aqueous sodium carbonate are given, and a method for the estimation of sparteine based on these data is described. W. G.

Condensation of Pyrrole with Methyl Ethyl Ketone, Methyl Hexyl Ketone, and with Acetone and Methyl Ethyl Ketone together; its Bearing on the Formulæ for Chlorophyll and Hæmin. V. V. TSCHELINCEV and B. V. TRONOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1197—1209. Compare this vol., i, 91, 93, 164).—The condensation of pyrrole with methyl ethyl ketone under the conditions previously employed yields: (1) a crystalline *compound*, $C_{32}H_{44}N_4$, m. p. 149·5—150·5°, having in freezing benzene the molecular weight corresponding with the above formula, and (2) a small proportion of a crystalline *isomeride*, m. p. 162°, having the correct molecular weight in freezing benzene. These compounds evidently contain four pyrrole

residues and four ketone residues in the molecule, and the pyrrole residues are regarded as connected in the 2- and 5-positions by way of the carbonylic carbons of the ketone residues (*loc. cit.*); if the methyl and ethyl groups of the ketone are able to occupy different positions, so as to give rise to cis-trans isomerism, four isomerides should be possible.

The above reaction was investigated by Dennstedt and Zimmermann (A., 1887, 598, 1052), who attributed to the resultant products the formulæ $(C_{16}H_{22}N_2)_3,5H_2O$ and $(C_{16}H_{22}N_2)_3,H_2O$. The authors show that such compounds do not exist, but that it is possible, on crystallisation from alcohol, to obtain an unstable compound, $C_{32}H_{44}N_4,2EtOH$, initial m. p. about 80°, which readily loses alcohol, and thus becomes converted into the compound, m. p. 149·5—150·5°. Dennstedt and Zimmermann's compound, $(C_{16}H_{22}N_2)_3,5H_2O$, is regarded as $C_{32}H_{44}N_4,2MeOH$.

Similar condensation of pyrrole with methyl hexyl ketone results in a small yield of a colourless, crystalline *compound*, $C_{48}H_{76}N_4$, m. p. 179°, which gives the normal molecular weight in freezing benzene. The principal product of the reaction is a viscous oil, which possibly contains others of the possible isomerides.

Condensation of pyrrole with acetone and methyl ethyl ketone simultaneously yields the crystalline *compound*, $C_{30}H_{40}N_4$, m. p. 203—204°, which exhibits the normal molecular weight in freezing benzene. The molecule of this compound evidently contains four pyrrole residues, two acetone residues, and two methyl ethyl ketone residues.

Constitutions are proposed for these products similar to that already suggested for the tetrapyrrole–tetra-acetone compound (*loc. cit.*), and it is shown that in the compounds obtained from methyl ethyl ketone, and from this together with acetone, the four iminic hydrogen atoms of the pyrrole residues in the molecule remain unreplaced. T. H. P.

Condensation of Pyrrole with *cyclo*Hexanone, other Cyclic Ketones, and Acetone and *cyclo*Hexanone together. Capacity of different Ketones for Condensation with Pyrrole. V. V. TSCHELINCEV, B. V. TRONOV, and S. G. KARMANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1210—1221).—The condensation of pyrrole with benzophenone (compare Tschelincev, Tronov, and Terentéev, A., 1915, i, 990) yields a product representing only the first stage of the condensation, in which for two molecules of pyrrole there is only one molecule of benzophenone, whereas when aliphatic ketones are used, more advanced condensation takes place. With the hope of obtaining intermediate products capable of throwing light on these condensations, the authors have made experiments with various cyclic ketones.

With *cyclo*hexanone, pyrrole yields the *compound*, $C_{20}H_{26}N_2$, which crystallises in slender needles, m. p. 272°, and has the normal molecular weight in freezing benzene. This compound is therefore simpler than those obtained with aliphatic ketones, as it contains only two ketonic residues and two pyrrole residues;

the two iminic hydrogen atoms in the latter are unsubstituted. With acetyl chloride at the ordinary temperature, it gives a deep red, solid product similar to that formed by the acetone condensation product, and with silver nitrate in alcoholic solution it yields the double *compound*, $C_{20}H_{26}N_2,AgNO_3$, as a white precipitate (compare Dennstedt and Zimmermann, A., 1887, 598, 1052).

With each of the three ketones, menthone, fenchone, and camphor, pyrrole is capable of condensing with greater or less rapidity, but the products obtained were oily or amorphous, and no pure individuals could be isolated.

When condensed with acetone and *cyclo*hexanone together, pyrrole yields: (1) the compound, m. p. 272°, obtained with *cyclo*hexanone alone; (2) the tetrapyrrole–tetra-acetone compound, m. p. 296° (compare this vol., i, 91); and (3) a *compound*, $C_{34}H_{44}N_4$, which forms crystals, m. p. 218—220°, and has the normal molecular weight in freezing benzene. This compound contains two *cyclo*hexanone residues, two acetone residues, and four pyrrole residues, but only two iminic hydrogens remain free; a structural formula in agreement with these facts is proposed.

The yields of condensation products formed by pyrrole with different ketones are as follows: with acetone, 93·5%; *cyclo*hexanone, 59%; methyl ethyl ketone, 54%; methyl hexyl ketone, 7%; and benzophenone, 3%. With the exception of *cyclo*hexanone, for which data are lacking, the above order is that of the higher atomicities of the oxygen atoms of these ketones, as measured by the thermal effects of their action on organo-magnesium alkyloxides. T. H. P.

Nitrosopyrrole-black. A. ANGELI and GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 273—278. Compare A., 1915, i, 912, 918, 1025).—When an aqueous solution of the sodium salt of *iso*nitrosopyrrole is treated with carbon dioxide, or when pyrrole reacts with ethyl nitrite or nitrous acid, a black powder, named *nitrosopyrrole-black*, is obtained. This product is almost insoluble in all solvents, but dissolves easily in alkali and is reprecipitated by acid; in alkaline solution it is instantly oxidised by permanganate and is decolorised by reducing agents, the dark colour subsequently reappearing in the air. The composition agrees approximately with the formula $(C_4H_3ON_2)_n$. Nitrosopyrrole-black does not melt, but at a high temperature deflagrates with liberation of red vapours.

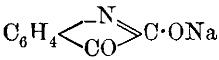
This compound appears to be accompanied by another, also black, which has not yet been investigated.

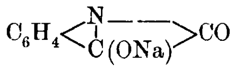
In nitrosopyrrole-black the CO-group of pyrrole-black is replaced by NO: $(C_4N)CO \longrightarrow (C_4N)NO$. T. H. P.

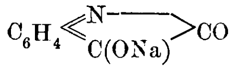
Constitution of the Blue Isatin Salts. M. CLAASZ (*Ber.*, 1917, **50**, 511—515).—In his discussion on the constitution of the salts of isatin and its derivatives, Heller declared that the different colours of the salts were due to the different attachments of the metal, the *N*-salts being deeper in colour than the *O*-salts, and he

suggested that this kind of isomerism should be taken into account in other cases (this vol., i, 219). It is now stated that the question can be very easily solved by taking cognisance of the stability of the salts towards water, for no cases of *N*- or *C*-metallic salts are known which are stable towards water. Isatin gives a blue salt which is soluble in water and therefore can only be an *O*-salt. Heller furthermore criticised as unnecessary Claasz's new betaine-like formula for indigoid substances (A., 1916, i, 839), but this actually helps to explain the relationships in the case of isatin, whereas Heller's theory is untenable.

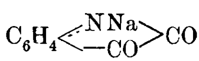
Isatin can give three *O*-salts, thus:

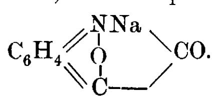

(I.)


(II.)


(III.)

Of these, salt II is the red salt of the red isomeride of isatin, namely, isatol, the discovery of which by Heller is a real contribution to the difficult problem. The blue salt, III, is soluble in water and owes its enhanced colour to the multiplication of chromophores; it is quinonoid. The deep blue *N*-sodium salt of isatin changes to red with water, owing to conversion into an *O*-salt. Its colour cannot be due only to the attachment of the metal, as there is a blue *O*-salt as well; neither can Heller's formula, IV, explain it, for this contains no chromophores. The "internal-salt" formula, V, containing Claasz's indigo chromophore, is more plausible:


(IV.)


(V.)

J. C. W.

Intramolecular Rearrangements and Ring Closures with Derivatives of Benzoylacetamide. ANDREAS KNUST and OTTO MUMM (*Ber.*, 1917, **50**, 563—574).—In an earlier paper (A., 1915, i, 244) it was shown that diacylamines can sometimes exist or behave in the unusual, but possible, form, R·C(:NH)·O·CO·R′. Compounds of this type can, of course, be prepared by the interaction of the sodium salt of an acid with an imide chloride, but it is not easy to say whether this structure is retained or whether rearrangement into the true diacylamine, R·CO·NH·CO·R′, takes place unless the product is capable of some indicative change. The most promising imide chlorides and acids to work with are those that offer opportunities for intramolecular ring closures, and the investigation already opened has now been advanced considerably in this direction. The methosulphate of 5-phenyl*iso*oxazole is readily obtainable, and is known to react with the salts of organic acids as though it were benzoylacetmethylimide sulphate, $COPh{\cdot}CH_2{\cdot}C(\frac{1}{2}SO_4){:}NMe$, that is, as a compound containing a reactive methylene and a ketone group. This agent has therefore been used extensively in the present investigation.

A concentrated aqueous solution of the agent reacts with sodium

pyruvate to form *benzoylmethylmaleimethylimide* [2 : 5-*diketo*-4-*benzoyl*-1 : 3-*dimethyl*-2 : 5-*dihydropyrrole*], $NMe<\begin{matrix}CO\cdot CBz\\ \quad\| \\ CO\cdot CMe\end{matrix}$, which crystallises in slender needles, m. p. 247°. Sodium cinnamate yields *benzoylacetylcinnamoylmethylamine*,

$$CHPh:CH\cdot CO\cdot NMe\cdot CO\cdot CH_2Bz,$$

m. p. 97°, which gives the methylamide of cinnamic acid, m. p. 111°, on boiling with dilute alcoholic hydrochloric acid. Sodium aminoacetate yields 2-*benzoylmethyl*-1-*methylglyoxalone*,

$$CH_2Bz\cdot C\lessgtr\begin{matrix}N\text{---}CH_2\\ NMe\cdot CO\end{matrix},$$

m. p. 219°, which has acidic properties. Sodium malonate forms *β-phenylglutaconmethylimide* (2 : 6-*diketo*-4-*phenyl*-1-*methyl*-1 : 2 : 3 : 6-*tetrahydropyridine*) in yellowish-brown crystals, m. p. 164°. This can be titrated as an acid, but it also forms an unstable *hydrochloride*, m. p. 204°, and *sulphate*, m. p. 256°.

In all these cases, therefore, the original *O*-acyl derivative has only a transitory existence. The isolated compounds are the products of subsequent ring closures of the diacylamines.

The above reagent also combines with phenol in a strong solution of sodium hydrogen carbonate, giving *phenyl methyliminobenzoylacetate*, $CH_2Bz\cdot C(:NMe)\cdot OPh$, in white, rhombic crystals, m. p. 100°. This ester cannot be rearranged into methylbenzoylacetanilide, but it readily yields phenol on boiling with alcoholic hydrochloric acid.

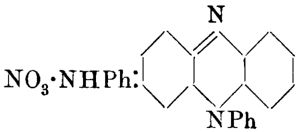
With potassium cyanate, the product is 4-*amino*-5-*benzoyl*-1-*methyluracil*, $NH_2\cdot C\lessgtr\begin{matrix}CBz\cdot CO\\ NH\cdot CO\end{matrix}\gtrless NMe$, which forms unstable salts with acids (*acetate*, white needles, m. p. 302°; *hydrochloride*, leaflets; *nitrate*, large octahedra), and also yields a *potassium* salt and is converted into the 1 : 3-*dimethyl* compound, broad needles, m. p. 250°, by means of methyl sulphate. The mother liquor from the crystallisation of the product from glacial acetic acid contains a small quantity of 4-*phenyl*-1-*methyluracil*, which separates from alcohol in stout, rhombic crystals, m. p. 221°, forms a *hydrochloride* with the same m. p., but does not dissolve in sodium hydroxide.

Ethyl sodiomalonate yields the enolic form of *ethyl methyliminobenzoylacetylmalonate*, $OH\cdot CPh:CH\cdot C(:NMe)\cdot CH(CO_2Et)_2$, in long needles, m. p. 121°, which is hydrolysed and condensed by boiling with alcoholic potassium hydroxide to 4-*methylamino*-6-*phenyl*-1 : 2-*pyrone*-3-*carboxylic acid*, $NHMe\cdot C\lessgtr\begin{matrix}CH{=\!=}CPh\\ C(CO_2H)\cdot CO\end{matrix}\gtrless O$, m. p. 201°, and this loses carbon dioxide when heated at 205°, forming 4-*methylamino*-6-*phenyl*-1 : 2-*pyrone*, m. p. 180° (*hydrochloride*, m. p. 117°). Ethyl sodioacetoacetate yields 4-*methylamino*-3-*acetyl*-6-*phenyl*-1 : 2-*pyrone*, in rhombic leaflets, m. p. 161°, which are quite neutral.

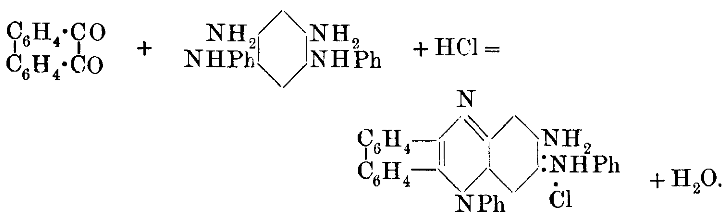
J. C. W.

Azine Dyes. F. Kehrmann (*Ber.*, 1917, **50**, 554—563).—[With René Speitel.]—*Phenyl*apo*safranine*.—This dye is most conveniently prepared by eliminating the amino-group in *ψ*-mau-

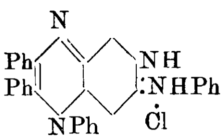
veine through the diazo-reaction, the latter compound being obtained by oxidising a mixture of *p*-phenylenediamine and diphenyl-*m*-phenylenediamine. The nitrate (annexed formula) crystallises in very long, brassy needles. When boiled with aniline and aniline hydrochloride, phenyl*apo*safranine yields the insoluble chloride of 2:3-dianilino-10-phenylphenazine and a small quantity of the soluble, blue chloride of 2:8-dianilino-10-phenylphenazine (diphenylphenosafranine. Compare A., 1898, i, 153).



[With MAX WEILENMANN.]—*Constitution of the Anilino-derivative of 2-Aminoflavinduline.*—When 2-aminoflavinduline chloride is treated with aniline it yields the chloride of 2-amino-3-anilinoflavinduline (A., 1900, i, 255). The proof for this constitution is that the dye can be obtained by condensing phenanthraquinone with 4:6-dianilino-*m*-phenylenediamine, thus:

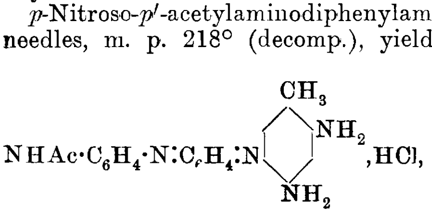


A similar condensation has been effected with benzil. The *product* (annexed formula) crystallises in metallic-green needles; the free *base* forms green leaflets, m. p. 235°; the *nitrate* forms brassy needles; the *platinichloride* is an almost insoluble, dark red, bronzy powder, and the *dichromate* is an insoluble, reddish-brown powder.



[With WLADISLAUS POPLAWSKI.]—*Some New Indamines.*—It was hoped that by introducing aryl groups into the amino-group of an indamine, some improvement in the tinctorial value of these compounds might be effected. Some new indamines of the type of tolylene-blue have accordingly been prepared, using nitroso-derivatives of diphenylamines instead of the usual dimethylaniline, but the dyes are not sufficiently fast to acids or light to make them of any real value.

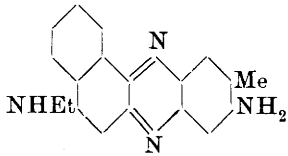
p-Nitroso-*p'*-acetylaminodiphenylamine, glistening, reddish-brown needles, m. p. 218° (decomp.), yields with *m*-tolylenediamine a dark blue *indamine* of the annexed formula when the alcoholic solutions are warmed at 30° for some time with a little acetic acid, whilst at 60° the *p*-acetylamino-group is re-



placed by hydrogen and a similar blue *indamine* is formed. *p*-Nitrosoethyl-*p*-sulphobenzylaniline yields an *indamine* of the formula A, whilst nitrosoethyl-*α*-naphthylamine does not form an indamine, but the corresponding metallic-green *hydrochloride* of the *azine*, B:

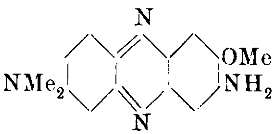
$C_6H_4{\cdot}CH_2{\cdot}NEt{:}C_6H_4{:}N{\cdot}C_6H_2Me(NH_2)_2$
SO_2———O

A.



B.

6-Methoxy-*m*-phenylenediamine (2:4-diaminoanisole) reacts with *p*-nitroso-*p'*-acetylaminodiphenylamine to form a violet-blue *indamine*, $C_{21}H_{21}O_2N_5,HCl$, and with *p*-nitrosodimethylaniline to form the brownish-red *azine*, m. p. 258°, of the annexed formula. This can be methylated by means of methyl sulphate, and the product forms a *platinichloride*, $C_{32}H_{36}O_2N_8,H_2PtCl_6$. J. C. W.



Acylsemicarbazides and Acylsemicarbazic Acids. J. Bougault (*Compt. rend.*, 1917, **164**, 820—822).—A comparison of the benzoylsemicarbazide prepared from phenylglyoxylic acid (compare A., 1916, i, 764, 765) with that obtained by Widman and Cleve (compare A., 1898, i, 335) from benzoic anhydride and semicarbazide. The latter compound is acidic in character and is considered to be the isomeride (I), whilst the semicarbazide obtained from phenylglyoxylic acid is considered to be the isomeride (II).

(I) $OH{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$.
(II) $O{:}CPh{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$.

Compounds of the type I, which are acidic, are obtained by the action of semicarbazide on acid anhydrides or chlorides, and for these the author suggests the name acylsemicarbazic acids, to distinguish them from compounds of the type II, which are basic and can only be obtained by the action of iodine and sodium carbonate on the semicarbazones of *α*-ketonic acids. W. G.

Oxidation of Phenylazocarbonamide. A. Angeli (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 207—213).—The azoxy-compound obtained (this vol., i, 228) by oxidising phenylazocarbonamide by means of hydrogen peroxide yields nitrogen and phenol when boiled with 25% sulphuric acid solution, evidently by way of phenylazocarboxylic acid and benzenediazonium sulphate. It is highly sensitive to the action of alkali hydroxide or carbonate, addition of a few drops of sodium carbonate solution to a boiling aqueons solution containing the amide and *β*-naphthol resulting in the immediate appearance of the scarlet coloration characteristic of benzeneazo-*β*-naphthol.

Since phenylazoxycarbonamide remains unchanged when treated at the ordinary temperature with bromine in the absence of any solvent, its structure is regarded as represented by the formula $O:NPh:N\cdot CO\cdot NH_2$, and not by $NPh:NO\cdot CO\cdot NH_2$. It is isomeric with, but much more stable than, the nitrosoamine of phenyl carbimide, $NH_2\cdot CO\cdot NPh\cdot NO$, which yields nitrogen and phenol when boiled with water. On reduction, phenylazoxycarbonamide is converted into the original phenylazocarbonamide (compare Widman, A., 1895, i, 603). T. H. P.

p-, *o-* **and** *m-***Tolueneazo-**α**-naphthylhydrazinesulphonic Acids.** J. Tröger and G. Lange (*Arch. Pharm.*, 1917, **255**, 1—7) —It has already been shown that under suitable conditions benzene diazonium salts can be converted into the corresponding hydrazinesulphonic acids by the action of sulphur dioxide on the aqueous solution, aminoazobenzene after diazotisation being convertible by this process into benzeneazophenylhydrazinesulphonic acid, $N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$ (Tröger and Puttkamer, A., 1907 i, 263; Tröger and Westerkamp, A., 1910, i, 207), and the authors have now extended this reaction to the diazo-compounds derived from the tolueneazo-α-naphthylamines.

p-Tolueneazo-α-naphthylamine (Weselsky and Benedict, *Ber.* 1879, **12**, 229) when diazotised at 20° yields an insoluble, brown solid, together with the solution of the diazo-compound, the latter on addition to a solution of potassium sulphite and potassium carbonate undergoing conversion into *potassium* p-*tolueneazo-α-naphthalenediazosulphonate*, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot SO_3H$; this separates in a labile, reddish-brown modification, which shortly becomes deep brown. When warmed with ammonium sulphide in aqueous solution, the potassium diazosulphonate is reduced to the *potassium* salt (brown needles) of p-*tolueneazo-α-naphthylhydrazinesulphonic acid*, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H$, the free acid when dry forming a violet-black powder. This sulphonic acid when mixed with an aromatic aldehyde and a little alcoholic hydrogen chloride is capable of giving condensation products with elimination of the sulphonic acid group; by this reaction there were obtained p-*tolueneazo-α-naphthylsalicylidenehydrazine*,

$$C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH,$$

deep red prisms, m. p. 166·5° (*hydrochloride*, deep green, crystalline powder); p-*tolueneazo-α-naphthylcinnamylidenehydrazine* $C_6H_4Me\cdot N:N\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot CH:CHPh$, deep reddish-brown prisms, m. p. 168·5° (*hydrochloride*, black powder with green lustre; p-*tolueneazo-α-naphthylanisylidenehydrazine*,

$$C_6H_4Me\cdot N:N\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4\cdot OMe,$$

brown crystals, m. p. 156° (*hydrochloride*, greenish-black crystals) p-*tolueneazo-α-naphthyl*-p-*tolylidenehydrazine*,

$$C_6H_4Me\cdot N:N\cdot C_{10}H_6\cdot NH\cdot N:CH\cdot C_6H_4Me,$$

brownish-black prisms, m. p. 159° (*hydrochloride*, bluish-black crystals).

o-*Tolueneazo-α-naphthylamine*, $C_6H_4Me\cdot N_2\cdot C_{10}H_6\cdot NH_2$, red silky needles, m. p. 99° (*hydrochloride*, bluish-violet needles

sulphate, pale violet needles with $3H_2O$; *nitrate*, greenish-black crystals), prepared by the interaction of an aqueous diazotised solution of *o*-toluidine and alcoholic α-naphthylamine, was by the usual process of diazotisation and subsequent treatment with alkaline sulphite solution converted into brown *potassium* o-*tolueneazo-α-naphthalenediazosulphonate*, which on reduction with ammonium sulphide yielded brown, silky needles of the *potassium* salt of o-*tolueneazo-α-naphthylhydrazinesulphonic acid*, $C_6H_4Me\cdot N{:}N\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H$. The violet-black, free acid, like its para-isomeride, reacted with aldehydes in the presence of alcoholic hydrogen chloride, with formation of arylidene derivatives of the corresponding *o*-tolueneazo-α-naphthylhydrazine; o-*tolueneazo-α-naphthylsalicylidenehydrazine*, deep brown crystals, m. p. 162° (*hydrochloride*, bluish-green powder); *cinnamylidene* compound, brown prisms with green lustre, m. p. 170° (*hydrochloride*, black, crystalline powder); *anisylidene* compound, brown leaflets, m. p. 153° (*hydrochloride*, dark blue leaflets); p-*tolylidene* compound, brown crystals, m. p. 152° (*hydrochloride*, black, crystalline powder).

m-*Tolueneazo-α-naphthylamine*, red crystals with blue lustre, m. p. 107° (*nitrate*, bluish-violet needles; *hydrochloride*, black, silky needles with $2H_2O$; *sulphate*, blue prisms), was prepared by the gradual addition of a solution of *m*-toluenediazonium chloride co an alcoholic solution of α-naphthylamine at 45°. In an analogous manner to its preceding *o*- and *p*-isomerides, this substance was successively converted into reddish-brown *potassium* m-*tolueneazo-α-naphthalenediazosulphonate* and *potassium* m-*tolueneazo-α-naphthylhydrazinesulphonate*, reddish-brown needles. The free *m*-tolueneazo-α-naphthylhydrazinesulphonic acid forms violet flocks and reacts with anisaldehyde and alcoholic hydrogen chloride, yielding m-*tolueneazo-α-naphthylanisylidenehydrazine*, a brown, crystalline powder, m. p. 159—160°; *hydrochloride*, bluish-black, crystalline powder. D. F. T.

Physical Changes in the Condition of Colloids. XXI. Protein Silver Salts. WOLFGANG PAULI and JOHANN MATULA (*Biochem. Zeitsch.*, 1917, **80**, 187—210).—The combination of proteins with silver salts was investigated by two methods, which gave parallel results, (*a*) by electrometric measurement of the changes in the Ag˙ concentration (in concentration cells), (*b*) by measurement of changes in electrical conductivity when proteins are added to silver salts. The changes were measured when different amounts of proteins were added to the same silver solution and when the same amount of protein solution was mixed with silver nitrate solutions of varying concentration. The proteins used were gelatin, serum-albumin (ox), and caseinogen. The results indicate a combination of the protein with silver nitrate. The amount of silver salt taken up from a given solution is not directly proportional to the amount of protein added, and the results obtained indicate a hydrolytic dissociation of the silver salt protein. The reaction appears to be a reversible one, like

that of the alkali salt–protein combination, and this statement receives confirmation from the fact that less silver salt is taken up by the protein in the presence of a salt of an alkali. Furthermore, the maximal amount of potassium chloride taken up by gelatin in a 1% solution is equal to about $2 \cdot 2 \times 10^{-4}$ gram equivalents of chlorine per gram of the protein, and about the same maximal amount of silver is taken up. Heated serum albumir combines with a larger amount of silver salt up to the concentration of $0 \cdot 05N$-solution, but the maximal amount found is the same as that of the unheated albumin solution. The silver salt–proteir combination wanders to the anode in an electrical field in the same way as pure proteins. The conclusion is drawn that in the formation of combinations of proteins with silver salts and salts of alkalis and alkaline earths, the anionic and cationic parts are taken up in equivalent quantity by the proteins. In the formation of the insoluble protein–silver salt combination with albumin, severa molecules of the silver salt are taken up by each molecule of protein before the insoluble precipitate is formed. S. B. S.

Specific Behaviour of Proteins. E. HEKMA (*Int. Zeitsch phys.-chem. Biol.*, 1917, **3**, 122—132. Compare Diesselhorst and Freundlich, this vol., i, 180).—The author regards the specific behaviour of fibrin and other proteins as due to the property o existing in two forms, namely: (1) in an anisotropic, amorphous and (2) in an anisotropic, liquid micellar-crystalline condition When fibrin is placed in dilute alkali or acid, the swelling which occurs is caused by an adsorption of water into the molecules of fibrin, and the gradual passage of the fibrin gel into solution in regarded as the result of a change in the individual fibrin molecules from an isotropic solid to an anisotropic liquid-crystallin state. H. W. B.

Interesting Property of Old Solutions of Fibrinogen P. NOLF (*Ann. Inst. Pasteur*, 1917, **31**, 155—160).—If a solution of fibrinogen is kept at 0° for some time, it gradually loses the property of clotting on the addition of fresh serum or a solution of thrombin. The clotting property is retained more readily by concentrated solutions of fibrinogen; dilute solutions, or those containing a trace of sodium carbonate, may lose the property within a few days, or at latest within three or four weeks. The los of clotting power occurs in stages; the clot formed after the first few days is found to be more flabby, tending to become viscous and finally fails to become visible. This result is not due to the action of bacteria, since fibrinogen solutions can be kept at 0° for several months without betraying any sign of putrefaction.

The author explains the phenomenon by assuming that a gradua increase occurs in the stability of the fibrinogen molecules. Combination still ensues between thrombin and the stabilised fibrinogen since a solution of the latter is found to possess distinct ant clotting power, which is apparently to be ascribed to the capacit for withdrawing thrombin by adsorption without any formatic

of fibrin. Moreover, by warming to 56°, which coagulates fibrinogen, the anti-clotting property disappears.

The hypothesis of the gradual transformation of one of the necessary factors in fibrin formation into an anti-clotting factor offers an explanation of the phenomena associated with the production of anti-clotting substances in the animal organism. The anti-substance present in peptone plasma, for instance, may be derived from fibrinogen. It is not stabilised fibrinogen, because its anti-clotting power is much greater and is not inhibited at 56°. The author, however, suggests that the liver may secrete a series of substances allied to fibrinogen possessing a common affinity for thrombin, but differing in solubility, molecular size, and temperature of coagulation. Substances opposing fibrinolysis would also be included in this series. H. W. B.

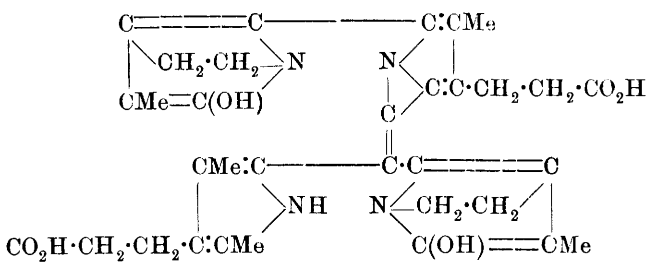
Helicorubin. CH. DHÉRÉ and G. VEGEZZI (*Compt. rend.*, 1917, **164**, 869—870).—In addition to the two bands already known in the absorption spectrum of alkaline helicorubin, the authors have discovered a third band at $\lambda = 427\ \mu\mu$. Acidified helicorubin has a similar spectrum, except that the first band is twinned. When helicorubin, in acid solution, is shaken with air, it is oxidised, and the product has an absorption spectrum different from that of the original substance. It shows three bands: (1) from λ 580 to λ 563, (2) from λ 547 to λ 519, and (3) at $\lambda = 415\ \mu\mu$. When helicorubin is acted on by acidified alcohol, it gives a helicohæmatin, which, when reduced in alkaline medium, gives a typical hæmochromogen. If helicorubin is oxidised by potassium permanganate and then reduced, the product shows an absorption band in the yellow at $\lambda = 587\ \mu\mu$. With acetic or tartaric acids in the presence of sodium hyposulphite, helicohæmatin gives hæmatoporphyrin. Helicorubin is thus closely related to hæmoglobin, and acts without doubt in the intestine of the snail as a respiratory pigment. W. G.

Bile Pigments. X. Bilirubin-ammonia and Modifications of Bilirubin. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1917, **99**, 86—130. Compare A., 1915, i, 829).—The author describes a method for removing the compound containing sulphur which has been shown by Fischer (A., 1916, i, 515) constantly to occur in crystalline bilirubin as ordinarily prepared from the gall-stones of the ox. Bilirubin-ammonia is first formed by the action of ammonia in dry methyl alcohol (*loc. cit.*). Two modifications of this substance are observed, the one, *A*, crystallising directly from the cold methyl alcohol solution, and the other, *B*, being precipitated from the mother liquor by ether. Bilirubin-ammonia-*A* is a stable substance and decomposes only slowly at 90°. The *B* modification is unstable and quickly undergoes oxidation at the ordinary temperature, forming a brown mass. On boiling with chloroform or extracting with chloroform vapour, both modifications yield bilirubins of slightly different properties which are designated bilirubin-*A* and -*B* respectively. At the same time, a

residue remains insoluble in chloroform, the amount of which is larger when the *B* form of bilirubin–ammonia is employed, but in both cases is found to be larger the longer the respective specimens of bilirubin–ammonia-*A* and -*B* have been kept. This insoluble substance contains the impurity shown by Fischer to be present in ordinary crystalline bilirubin; both bilirubin-*A* and -*B* are free from sulphur.

On analysis, bilirubin-*A* and bilirubin-*B* are both found to contain traces of chlorine derived from the chloroform used in their isolation. They are therefore again treated with ammonia and methyl alcohol, and the resulting ammonia compounds decomposed by boiling methyl alcohol. In this way two bilirubins, *A A* and *B B*, are prepared, giving figures on analysis which agree with the formula $C_{33}H_{36}O_6N_4$, originally proposed by Fischer, which is now definitely accepted by the author. The second of these bilirubins is even more easily oxidised and decomposed than bilirubin-*B*. Apparently the *A*-modification becomes partly converted into the *B* under the influence of ammonia, whilst the reverse change of *B* into *A* is favoured in the presence of chloroform. Between the orange *A* and the red *B* forms there are possibly several intermediate bilirubins.

From a consideration of the properties of and transformations undergone by bilirubin and its derivatives, the author is led to propose the following revised structural formula for the substance:



Corresponding formulæ are drawn for mesobilirubin, mesobilirubinogen, the xanthobilirubic acids, and other derivatives of bilirubin. H. W. B.

Optical and other Properties of Pancreatin. M. A. RAKUZIN and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1314—1315).—Pancreatin, which exhibits both diastatic and peptonising properties, is usually regarded as a mixture of trypsin and diastase. This view is, however, not supported by the colour reactions of the three enzymes, and no decision is possible by means of the optical activity, since none of these enzymes is active. Pancreatin is adsorbed both by the electro-negative kaolin and, about twice as strongly, by the electro-positive aluminium hydroxide. Both adsorptions are irreversible, and both precipitate and filtrate exhibit the same colour reactions as the original pancreatin. At present it is, therefore, impossible to decide

if the adsorption is selective or non-selective, but further work in this direction is in progress. T. H. P.

The Inhibition of the Single Amyloclastic Functions of Amylase of Malt Produced by Keeping in the Presence of Various Reagents. T. CHRZĄSZCZ and A. JOSCHT (*Biochem. Zeitsch.*, 1917, **80**, 211—241).—The action of malt amylase is regarded by the authors as being compounded of the action of two distinct ferments, one producing the liquefaction of starch, and the other its degradation to sugars. The production of dextrins (as determined by the iodine reaction) is either a resultant of the action of these two enzymes or is due to a special ferment. The method of experiment adopted was the determination of these various reactions with a sample of malt ferment which had been kept for various intervals in the presence of different reagents. The dextrinising action is inhibited in some cases more strongly, the more strongly is inhibited the liquefying action, whilst in other cases the inhibition runs more nearly parallel with the inhibition of the saccharifying power. For this reason, Wohlgemuth's iodine method for determining amyloclastic activity is open to objections, as amylase cannot be regarded as a single enzyme. For the preparation of amylase extracts, glycerol in appropriate concentration in water, and aqueous solutions of pyridine and quinoline are most suitable, as they cause the smallest amount of inhibition of the various amyloclastic functions when the ferment preparation is kept for a long time in their presence. Pure water, solutions of alcohols, acetone, and chloroform are not suitable. Bases in suitable concentrations have a favourable action on the liquefying and dextrinising functions, but inhibit the saccharifying function. Alcohols inhibit all functions, but more especially the liquefying and dextrinising. S. B. S.

Mechanism of Oxydase Action. G. B. REED (*Bot. Gaz.*, 1916, **62**, 53—64).—There exists a considerable body of data which indicates that all oxydases are made up of two constituents: a peroxide-like substance or oxygenase and a substance capable of activating this peroxide or a peroxydase. Further light has been thrown on the reaction by investigating the effect of platinum-black as a catalyst. A large platinum crucible was coated with a deposit of the colloidal metal and exposed to nascent oxygen by making it the anode in a dilute solution of hydrochloric acid through which an electric current was passed. The crucible was then immersed in the solution to be oxidised. Oxidation took place in proportion to the amount of oxygen furnished by the charged platinum and additive effects were obtained by removing and recharging the crucible. As a basis of comparison, the rate of oxidation was next determined, when hydrogen peroxide was used as an oxidising agent and platinum-black as a catalyst. In comparing the curves for the rate of oxidation obtained by the two methods, it became evident that by starting with a sufficient charge of oxygen on the platinum-black and by renewing it often enough,

the curves could be made exactly similar. It appeared likely, therefore, that the hydrogen peroxide acted by continually recharging the platinum-black with oxygen, and this hypothesis was fully confirmed by following out the variations in oxidation potential which occurred in the different phases of the reaction.

L. M. U.

Mode of Action of Plant Peroxydases. G. B. Reed (*Bot. Gaz.*, 1916, **62**, 233—238).—Following on the lines of the previous experiments, the platinum-black was replaced by a plant peroxydase. About 150 grams of finely chopped horseradish root were extracted with 300 c.c. of water. The solution behaved like the platinum-black: alone it produced no oxidation, but as soon as it was charged with oxygen by treatment with potassium permanganate, oxidation occurred in the measure of the charge, and additive effects were obtained by treating the peroxydase solution a second time with potassium permanganate. Potato peroxydase gave exactly similar results, and the author concludes that in oxidation processes catalysed by peroxydases, two reactions are involved: the peroxydase combines with oxygen from the oxygenase to form an intermediate compound which is a more energetic oxidising agent than the original source of the oxygen. L. M. U.

The Relation between Oxydase and Catalase in Plant Tissues. G. B. Reed (*Bot. Gaz.*, 1916, **62**, 409—412).—Although peroxydases usually decompose hydrogen peroxide, the experiments with platinum-black (see preceding abstracts) would indicate that the action of the peroxydase is independent of its ability to decompose hydrogen peroxide. In order to throw more light on the question, pineapple juice was pressed out of fruits at different stages of ripeness, and was examined for catalase and peroxydase activity. Catalase activity was measured by the direct decomposition of hydrogen peroxide, whilst peroxydase activity was measured by the oxidation of pyrogallol by hydrogen peroxide. Different fruits exhibited great variation in their catalase activity, but scarcely any in their peroxydase activity. The author therefore concludes that the substances which effect the decomposition of hydrogen peroxide are not of necessity concerned with the enzymes which accelerate peroxide oxidations. L. M. U.

Significance of Colour Changes in Oxydase Reagents. Separation of Oxydase Reactions from the Catalase Reaction. G. B. Reed (*Bot. Gaz.*, 1916, **61**, 430—432; **62**, 303—308; from *Physiol. Abstr.*, 1917, **2**, 197, 198).—The author has compared the efficiency of the different colour reagents used for work on oxydases with regard to the amount of oxidation required to give an appreciable colour change. The volume of standard permanganate required to give the minimum colour change to $0·1M$-solution of reagent varied from 0·5 c.c. with dimethyl-*p*-phenylenediamine to 10·0 c.c. with quinol.

In the second paper the author opposes the view that the cata-

lase action, in which hydrogen peroxide is decomposed with liberation of molecular oxygen, is in any way causally associated with peroxydase decomposition of hydrogen peroxide in oxidation reactions. He finds that the two types of activity with colloidal platinum do not show any correlation. A colloidal platinum surface charged with hydrogen continues to decompose hydrogen peroxide much faster than if charged with oxygen, but as regards peroxydase activity, while oxidising formaldehyde in the presence of the peroxide, the platinum in its two states is identical. Measurement of the oxygen potentials of the two states shows that, whilst widely divergent in the first minute, they both shift to the same mean oxygen potential in a few minutes. G. B.

Periodic Phenomena shown by Ferments. J. TEMMINCK GROLL (*Arch. Néerland. Physiol.*, 1917, **1**, 403—424. Compare Arrhenius, *Immunochemie*, 1907).—The activity of urease at 35° when plotted against time gives a sinusoidal curve, the activity becoming alternately weaker and stronger. At 65° a unimolecular curve is obtained, as given by Arrhenius (*loc. cit.*). At intermediate temperatures (45—55°) the curve is a combination of the two. It is suggested that this is a consequence of the colloidal nature of the ferment, and in support of this view the catalytic decomposition of hydrogen peroxide by colloidal platinum and gold has been further examined. Definite results could not, however, be obtained, as the oscillation of the activity of these catalysts is so rapid that the phenomenon is not clear. W. G.

Physiological Chemistry.

The True Nature of the "Acidotic Condition" of Infants. K. A. Hasselbalch (*Biochem. Zeitsch.*, 1917, **80**, 251—258).—In attempting to ascertain the true reaction of the blood in the diagnosis of acidotic conditions, care should be taken to make the estimation in the presence of a sufficient tension of carbon dioxide. If this is not done, the concentration of the oxyhæmoglobin will be the most important factor in the result, as it is a fairly strong acid. From the point of view of these facts, the author criticises some conclusions drawn by Ylppö on the supposed acidosis in new-born infants, in which the precaution above mentioned was neglected; the author contends, therefore, that this acidosis of the new-born infant does not exist. S. B. S.

The Ammonia Content of the Blood. II. V. Henriques and E. Christiansen (*Biochem. Zeitsch.*, 1917, **80**, 297—311).—When ammonia is estimated in the blood by Folin's aeration

method, care must be taken not to allow the temperature to rise too high. If the temperature is maintained below 20°, the same amount of ammonia is obtained, whatever base is used to make the blood alkaline (sodium carbonate, lime water, or magnesium oxide). At higher temperatures (45°), however, larger amounts of ammonia are obtained when sodium carbonate is used. All bases give rise to more ammonia from the blood at 45° than at 16°. The ammonia is obtained in larger quantities from the corpuscles than from the plasma. The quantity of ammonia in the case of carnivorous animals is larger in the blood of the portal vein than in the blood of the arteries, even when the animals have fasted for eight days. This marked difference is not observed in the case of dogs. Arterial and venous bloods contain the same amount of ammonia. S. B. S.

Experimental Glycosuria. XII. Production of Lactic Acid in the Blood following the Injection of Alkaline Solutions of Dextrose or of Alkaline Solutions alone. J. J. R. Macleod and D. H. Hoover (*Amer. J. Physiol.*, 1917, **42**, 460—465; from *Physiol. Abstr.*, 1917, **2**, 119. Compare this vol., i, 367).—The control of the blood sugar level is effected, not by changes in the glycogenic function in liver and muscles, or by oxidation of the dextrose in the muscles, but by destruction of the sugar in the blood itself. Samples of blood collected in different parts of the circulation show that lactic acid increases there when alkaline solutions, but not when acid solutions, of dextrose are injected. Some enzyme in the blood, of the glyoxalase class, is considered to be responsible for the change. G. B.

The Residual Reduction of the Blood Considered in Relationship to the Reducing Components of the Residual Nitrogen. Joh. Feigl (*Biochem. Zeitsch.*, 1917, **80**, 330—332).—Chiefly a discussion of the part played by creatine and creatinine in contributing to the "residual reduction" (of alkaline copper solutions, etc.) by the blood. S. B. S.

Prothrombin and Thrombin (Free and Combined) in Blood Serum. H. S. Gasser (*Amer. J. Physiol.*, 1917, **42**, 378—394; from *Physiol. Abstr.*, 1917, **2**, 115).—There is only one kind of thrombin; it may be formed from prothrombin (by calcium and thromboplastin) or liberated from combination with antithrombin by alkali activation. This inactive compound is believed to exist because (1) the inactivation of thrombin by non-specific colloids, such as charcoal, is negligible compared with that produced by plasma; (2) if serum is kept, both antithrombin and combined thrombin disappear at the same time; (3) combined thrombin is destroyed by heat at the critical temperature of antithrombin (not at that of thrombin); (4) in alkali activation, thrombin is destroyed; (5) when thrombin is incubated with antithrombin (that is, plasma heated at 60°), a combination is formed which does not clot fibrinogen until activated by alkali. Thrombo-

plastin does not liberate combined thrombin. The amount of prothrombin in serum varies inversely as the amount of tissue extract present at the time of clotting. The amount of thrombin formed in the presence of a given amount of thromboplastic substance is definite in amount; it forms rapidly and is combined rapidly, the system then returning to equilibrium. This rapid inactivation by the plasma, which is intolerant of free thrombin, maintains the fluidity of the blood. G. B.

Applicability of Schulze's Law to Complement. E. Poyarkov (*C. R. Soc. de Biol.*, 1917, **80**, 239—241).—The action of complement is known to be slowed or inhibited by solutions of the salts of the alkaline earths. The author has investigated the complement of the spermolysin of normal rabbit's serum, and finds that the effect of neutral salts depends greatly on the valency of the cation. He has determined the concentrations of various salts which render the action of the complement most rapid; a concentration of 43—60 millimolecules of various sodium salts corresponds with 5—7 millimolecules for barium, strontium, and calcium chlorides, and with 0·2 millimolecule for aluminium chloride, and hence there is a close correspondence with the precipitation of lyophobic sols (for example, of arsenious sulphide). The author deduces from this applicability of Schulze's law that the complement is a negative suspension colloid, and therefore not a protein, but a lipoid. Among lipoids, lecithin does not obey Schulze's law, but cholesterol does. In general, the results support the colloidal theory of immunity (Bordet) rather than the physicochemical theory (Ehrlich, Arrhenius). G. B.

Production of Light by Animals. E. Trojan (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 94—105).—A discussion of the reasons why certain animals should emit light and of the possible ways in which the light is produced. H. W. B.

Bio-luminescence and Metabolism. Robert Heller (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 106—121).—The author advances the theory that the phenomenon of bio-luminescence is associated with the last phases in the catabolism of those nitrogenous substances which are eliminated as purines from the animal organism. According to his unpublished results, hypoxanthine, guanine, xanthine, theobromine, and other purines exhibit an intense photophosphorescence. H. W. B.

Selective Adsorption of Antidiphtheritic Serum by Aluminium Hydroxide. M. A. Rakuzin and G. D. Flier (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1324—1330).—It has been shown previously that the adsorption of enzymes and toxins, especially by aluminium hydroxide, is in most cases selective, and the investigations have now been extended to antidiphtheritic serum.

The serum employed, D^{15} 1·0340, $[\alpha]_D$ $-28·876°$, was straw-yellow and of neutral reaction. It gave the following protein

colour reactions, with the degrees of sensitiveness indicated in brackets: biuret (1:660), Millon's (1:330), Liebermann's (1:2500); Adamkiewicz's (1:9000), xanthoprotein (1:660), Molisch's (1:330), Pettenkofer's (1:1250), and Ostromisslenski's (1:1250). The adsorption by aluminium hydroxide proceeds irreversibly and with quantitative separation of the toxin, the proportion of the latter adsorbed being 43·47%. The liquid remaining after the adsorption is colourless and neutral, and gives all the above colour reactions of the proteins. T. H. P.

The Nature of Mountain Sickness. ERWIN RIPPSTEIN (*Biochem. Zeitsch.*, 1917, **80**, 163—186).—If rats are exposed in a chamber to diminished pressure, they exhibit symptoms analogous to those of mountain sickness. These appear when the air pressure is diminished to about 209 mm. of mercury (161·4 mm. reduced pressure), corresponding with the partial oxygen pressure of 27·68. If the chamber is filled with pure oxygen and the pressure is then diminished, the symptoms appear at the pressure of 91·25 mm. (41·25 mm. reduced), corresponding with the partial oxygen pressure of 23·48 mm. In experiments in which the air of the chamber was partly replaced by nitrogen and the pressure then diminished, the symptoms appeared at the pressure 459·90 mm., at which the partial oxygen pressure was 29·10. Carbon monoxide poisoning of moderate grade causes similar symptoms at ordinary barometric pressure. The conclusion is drawn that diminution of oxygen is the essential cause of mountain sickness, as the symptoms in all the experiments set in when the partial oxygen pressure was about the same, and the mechanical action on the lungs only appears when the barometric pressure is exceptionally low. S. B. S.

Selective Adsorption of Denys's Tuberculin by Aluminium Hydroxide. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1316—1319).—Two samples of tuberculin, prepared by (1) Vermel, Moscow, and (2) the Institut de Bactériologie de Louvain, have been examined. Both preparations are straw-yellow and neutral, and the other physical properties are: (1) D^{15} 1·0223, $c=6·3134$, $[\alpha]_D$ $-9·81°$, and (2) D^{15} 1·01944, $c=2·285$, $[\alpha]_D$ $-21·22°$. Both contain free ammonia and show Adamkiewicz's, Molisch's, Pettenkofer's, Ostromisslenski's, Liebermann's, and the xanthoprotein reactions, but the limits of sensitiveness differ widely in the two cases; only the Louvain preparation gives Millon's reaction, and neither gives the biuret reaction. Aluminium hydroxide adsorbs 7·62% and 23·08% of the respective preparations, and both adsorptions are irreversible as regards boiling water. With reference to the colour reactions of the proteins and to the rotatory power, the products of adsorption behave similarly to the original tuberculins. T. H. P.

The Resorption and Change of Abnormally Large Amounts of Sucrose and Invert-sugar. C. BRAHM (*Biochem. Zeitsch.*, 1917, **80**, 242—250).—Sugar was found neither in the

urine nor fæces after ingestion of as much as 300 grams of sucrose and invert-sugar (artificial honey) by man and dog. In one case as much as 600 grams were ingested in one day by a man, and even after this amount no sugar could be detected in the excreta.

S. B. S.

Intravitam Staining with Acid Dyes and its Significance for Anatomy, Physiology, Pathology, and Pharmacology. WERNER SCHULEMANN (*Biochem. Zeitsch.*, 1917, **80**, 1—142).—Two main problems have been considered by the author: (1) the rate of dissemination and elimination of the dyes after injection; (2) the storage of the dyes in the cells. Experiments have been carried out as far as possible with dyes of known and similar constitution, chiefly belonging to the trypan-blue and benzopurpurine groups and carbamide derivatives. There appears to be no relationship between chemical constitution and capacity for intravital staining, and the side-chain theory of Ehrlich will not explain the action of the dyes when injected into the living organism. On the other hand, experiments carried out for the author by Wilborn show that there is an intimate relationship between the rate of diffusion of dyes in gelatin gels and their capacity for intravital staining. Dyes which diffuse slowly are taken up chiefly by cells near the point of injection, whereas those which diffuse rapidly become quickly disseminated through the organism and eliminated. Other dyes have an intermediate character, and are disseminated with sufficient rapidity without being eliminated too quickly by the organism, and these are well adapted for intravital staining. The methods of taking up dyes and their storage by the cells are also discussed in great detail by the author, who directs attention to the relationship between amœboid movement, phagocytic action, and capacity for being stained by acid dyes, and the influence of surface tensions at interfaces and other physical characters on these factors. The nature of the "granula" and of "metachromatism" (the differences of colour of the dyes in different cells) is also discussed. Evidence is brought forward to show that "metachromatism" is due to the difference of the state of aggregation of the dyes under different conditions, such as the variation in the amount and character of the electrolytes. S. B. S.

Theoretical Considerations Relative to the Intravitam Staining with Acid Dyes. WERNER SCHULEMANN (*Kolloid Zeitsch.*, 1917, **20**, 113—118).—The author discusses the distribution of acid dyes in living organisms on the basis of experiments which are to be published elsewhere. The distribution is to a very large extent dependent on the physical condition of the dye in solution. The size of the particles not only affects the ultimate distribution, but also the rate at which the organism is coloured by the dye. The general coloration of an organism is apparently only attainable by the use of dyes which are molecularly disperse.

H. M. D.

The Physico-chemical Properties of the Products of the Group of the Arsenobenzenes. Their Transformation in the Organism. J. Danysz (*Ann. Inst. Pasteur*, 1917, **31**, 114—137).—From a study of the four compounds, diaminodihydroxyarsenobenzene, luargol, galyl (diphosphaminotetrahydroxyarsenobenzene), and novoarsenobenzene, it would appear that the first three have the characteristic properties of colloids, luargol being the most colloidal and galyl the least. Novoarsenobenzene possesses more the properties of a salt. The first three compounds when intravenously injected are converted into insoluble compounds, the precipitates thus formed being then redissolved by certain organic bases, giving stable, soluble compounds which are eliminated in the urine, this dissolution being probably largely controlled by the leucocytes. The last part of the paper is a summary of the present state of knowledge with reference to the toxicity of and intolerance for these compounds. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. II. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **80**, 357—363. Compare this vol., i, 305).—In continuation of the investigations on bacteria containing urease, it is shown by the author that these flourish and produce the enzyme when they are grown on Uschinski's medium when this contains traces of bouillon which is added to the medium in making the sub-culture of the bacteria originally grown on bouillon. In the absence of traces of this material, the bacteria remain alive and capable of reproduction, but their growth is considerably inhibited. Uschinski's medium contains glycerol, sodium and calcium chlorides, magnesium sulphate, dipotassium phosphate, ammonium lactate, and sodium aspartate. S. B. S.

The Effect of Some Acids and Alkalis on Soil Bacteria in the Soil Solution. OSWALD M. GRUZIT (*Soil Sci.*, 1917, **3**, 289—295).—A solution was extracted from a rich sandy soil by the paraffin oil method; from it were prepared three experimental solutions, one of which was made neutral, another alkaline ($N/446{\cdot}4$), and the third acid ($N/1200$), using sodium hydroxide and hydrochloric acid for the purpose. Ten c.c. of each solution were then inoculated into sterile sand and incubated, bacterial counts being made at intervals for two hundred and twenty days. In the alkaline medium the bacterial numbers remained nearly constant for eighteen days, then rose to about 150% of the original numbers; by the sixtieth day, when the medium gave an acid reaction, the numbers had fallen again to below the original level and continued to fall for another seventy days. In the neutral

medium, which had become acid on the eighteenth day, the numbers of bacteria decreased gradually from the very start until the fifth month. Finally, in the acid medium, the numbers fell rapidly to almost nothing and remained at a very low level for the whole two hundred and twenty days.

The experiment was repeated, using a solution from a sandy loam and sulphuric acid in the place of hydrochloric acid. The solutions in this case were made up to *N*/1200, *N*/1400, *N*/2164, and *N*/2840 acid and *N*/412, *N*/990, and *N*/1040 alkaline. Bacterial numbers in the alkaline media multiplied rapidly to between five and six times the original numbers, and then fell as before, the maximum point of development occurring a few days later with the two stronger than with the weaker solution. The *N*/2164 acid medium remained with approximately the same number of bacteria throughout the experiment, and stronger solutions caused immediate depression of bacterial numbers, but with the *N*/2840-acid the bacteria first increased to about three times their original numbers and then decreased. L. M. U.

Soil Bacteria and Phosphates. C. G. HOPKINS (*Science*, 1916, [*N.S.*], **44**, 246—249; from *Physiol. Abstr.*, 1917, **2**, 149).—Nitrite bacteria render soluble the phosphorus and calcium of insoluble phosphates in the process of converting ammonia into nitrite, corresponding with the equation $4HNO_2 + Ca_3P_2O_8 = CaH_4P_2O_8 + 2CaN_2O_4$. Neither ammonia-producing nor nitrate-producing bacteria have any appreciable effect in liberating soluble phosphorus. For full details see *Univ. Illinois Agric. Exper. Station Bull.* No. 190. G. B.

The Reducing Ferments. A. BACH (*Arch. Sci. phys. nat.*, 1917, [iv], **43**, 307—316).—The first part of the paper is a more detailed account of work already published (compare this vol., i, 375). The author notes the injurious effects of the aldehydes and of the products of reduction of the nitrates, notably hydroxylamine, on the catalytic power of the reducing ferment of milk. There are other factors which have not yet been elucidated. W. G.

Nitrification in Semi-barren Soils. W. P. KELLEY (*J. Agric. Research*, 1916, **7**, 417—437; from *Chem. Zentr.*, 1917, i, 679—680).—An account is given of laboratory and field experiments which have extended over a number of years. The experiments were performed partly according to a modification of Remy's solution process, but mainly with the soil itself, the latter serving as culture medium. Dried blood (13·20% N) in quantities varying from 0·0625 to 1%, bone meal (4·25% N) from 0·25 to 4%, and ammonium sulphate (21% N) from 0·0375 to 0·6%, were used as sources of nitrogen. Nitrates were generally estimated by the phenoldisulphonic acid process, sometimes also by reduction with aluminium; the methods yield concordant results. Experiments showed that the amounts of nitrate which are formed during four

weeks from blood, bone meal, and ammonium sulphate varied greatly with the differing concentrations, both with respect to the absolute amount and also to the proportion of nitrogen converted. Feeble or, in certain soils, negative nitrifying power was observed with 1% of blood, whilst, in the same circumstances, strong action was found with 1% of bone meal or 0·2—0·3% of ammonium sulphate. When, on the other hand, smaller concentrations of blood were used, such as are customary in field experiments, powerful nitrification was invariably caused. When equal amounts of nitrogen were employed, similar amounts of nitrate were formed whether from blood, bone meal, or ammonium sulphate. High concentrations of bone meal, with a nitrogen content corresponding with that of 1% of blood, have a more poisonous effect on nitrification than the latter. Experiments with widely differing varieties of soil from South California showed that the inability to nitrify 1% of blood is not limited to any particular variety of soil or to soils which have a low content of organic substances.

The addition of alkali salts caused divergent action according to the concentration of the source of nitrogen. In one soil, 0·05% of sodium carbonate was distinctly poisonous to the nitrification of 1% of blood, whereas 0·4% had no action towards 0·1% of blood. Similarly, 0·1% sodium carbonate was poisonous towards 0·15% ammonium sulphate, but distinctly stimulating to 0·0625%. It is further shown that very contradictory conclusions can be drawn from laboratory experiments when the period of action is altered. Nitrites were found in large quantity when excessive amounts of nitrogenous material were used; in certain cases the quantity of nitrite exceeded that of nitrate when the experiments were prolonged for several weeks. Addition of alkali salts can depress the formation of nitrates, whilst, at the same time, nitrites are produced. In the estimation of nitrate it is necessary to take the presence of nitrite into account, the error involved being much greater with the aluminium reduction method than with the other process. According to the author, it appears very probable that the results of previous investigations on nitrification are less valuable than those derived from experiments in which the conditions are made to approximate as closely as possible to those of field trials. (Compare Löhnis and Green, *Chem. Zentr.*, 1915, i, 497; Allen and Bonazzi, *Ohio Agr. Exp. Stat. Bull.*, 1915, **7**.) H. W.

The Apiculate Yeasts. E. Kayser (*Compt. rend.*, 1917, **164**, 739—741).—The apiculate yeasts are very resistant to acids, giving an active fermentation even in the presence of 2·5% of citric acid or 0·2% of sulphuric acid, but under such conditions they gradually lose, in successive generations, their characteristic form and become oval or round. The presence of acids thus favours their development in a must of beetroots and apples, and exerts a marked influence on the products of fermentation, giving more volatile products and less alcohol. Rise in temperature also causes the production of larger amounts of volatile esters. W. G.

Disinfection of Drinking-water: with a Description of a New Substance for the Preparation of Stable Tablets for the Sterilisation of Polluted Water. H. D. DAKIN and E. K. DUNHAM (*Brit. Med. Journ.*, 1917, i, 682—684).—Sodium *p*-toluenesulphochloroamide (chloroamine-T) (A., 1916, i, 533) only acts in acid solution at low concentrations, and tablets of this substance, mixed, for instance, with citric acid, are unstable on keeping. For this reason a carbonyl group has been incorporated in the molecule. p-*Dichloroamidosulphbenzoic acid*,

$$CO_2H \cdot C_6H_4 \cdot SO_2 \cdot NCl_2,$$

is prepared by oxidising *p*-toluenesulphonamide with sodium dichromate to *p*-amidosulphbenzoic acid and then chlorinating. The new substance, stout prisms from acetic acid, m. p. 213°, sterilises water in thirty minutes at a concentration of 1 : 300,000, and a solution of this strength is almost tasteless. It may be conveniently used as tablets containing 4% of the substance, 4% of sodium carbonate, and 92% of sodium chloride. One tablet, weighing 0·1 gram, would then sterilise 1 litre of water. G. B.

A Simple and Rapid Method of Studying Respiration by the Detection of Exceedingly Minute Quantities of Carbon Dioxide. A. R. HAAS (*Science*, 1916, [*N. S.*], **44**, 105—108).—In order to determine the effect of solutions on respiration, a new method has been devised for detecting minute quantities of carbon dioxide in solution. A piece of plant tissue is placed in a measured amount of the test solution with a given quantity of phenolsulphonephthalein as indicator, and the amount of carbon dioxide given off is measured by the colour developed. The method is extremely sensitive, rapid, and simple, and the amount of carbon dioxide given off in successive intervals can be estimated without disturbing the tissue. L. M. U.

Carbohydrate Metabolism in the Green Leaf. W. GAST (*Zeitsch. physiol. Chem.*, 1917, **99**, 1—53).—The author has estimated the dextrose, lævulose, maltose, and sucrose in the leaves of *Tropaeolum majus*, *Cucurbita ficifolia*, *Vitis vinifera*, *Musa Ensete*, and *Canna iridiflora* gathered at noon and shortly before daybreak, when the metabolic activities of the plants are at their highest and lowest points respectively.

In all cases, the sugar present in largest amount is sucrose. It reaches a maximum during the day and diminishes during the night. In *Canna*, sucrose constitutes 90% of the total sugars by night as well as by day. In the other cases, the percentage of sucrose is usually about 50 in the leaves taken at noon and between 40 and 45 in those gathered at night. Maltose, dextrose, and lævulose occur in varying proportions in different plants, and do not show any constant rise or fall during the twenty-four hours.

These results confirm those of previous workers, and are in accord with the view that the first recognisable product of assimilation in the green leaf is sucrose. H. W. B.

Nitrate and Nitrite Assimilation. XII. OSKAR BAUDISCH (*Ber.*, 1917, **50**, 652—660. Compare A., 1916, i, 699—702).—The author has already directed attention to the importance of organic complexes containing iron or magnesium in the processes of oxidation and reduction which go on in the living organism. He has now discovered that when a solution of a hexose or lactose is warmed with a small quantity of an iron salt and sodium carbonate, a dark brownish-reddish-violet solution may be obtained in which the iron does not react with hæmatoxylin, but which has specific reducing properties. For example, it reduces nitrobenzene to aniline, which the alkaline sugar solution alone will not do. Furthermore, it reduces nitrites, but not nitrates. The reduction is catalytic, for a small quantity of the iron solution reduces relatively large quantities of a nitrite, the products being ammonia and substances of the nature of aldehydic amines. The hypothetical acid, NOH, is again to be regarded as representing a critical, intermediate stage. J. C. W.

A Dynamical Theory of Antagonism. W. J. V. OSTERHOUT (*Proc. Amer. Phil. Soc.*, 1916, **55**, 533—553).—The electrical resistance of *Laminaria Agardhii* was determined in 0·52*M*-sodium chloride, in 0·278*M*-calcium chloride, and in various mixtures of these salts. In pure sodium chloride, the resistance fell from the first, but with all the other solutions, the resistance first rose and then fell. To account for this phenomenon, the author assumed: (1) that two processes were involved, and that the resistance was determined by a substance *M*, which was formed and broken down according to the reaction $A \longrightarrow M \longrightarrow B$; (2) that calcium chloride accelerated the reaction $A \longrightarrow M$; and (3) that both sodium chloride and calcium chloride combined with a substance in the protoplasm to form a compound which inhibited the reactions $A \longrightarrow M$ and $M \longrightarrow B$. Then, by ascribing suitable values to all the factors involved, theoretical curves of resistance were obtained which approximated closely to those plotted from the experimental results. The author points out that whether the assumptions do or do not represent actual facts, it is clear that there are two processes involved, one of which produces a rise and the other a fall of resistance, and that their speed may be regulated by varying the proportions of sodium chloride and calcium chloride. Further, the theory enables the resistance of cells to be predicted in any mixture of the salts and at any given time during exposure. L. M. U.

Antagonism and Weber's Law. W. J. V. OSTERHOUT (*Science*, 1916, [*N.S.*], **44**, 318—320).—The dynamical theory of antagonism (outlined above) is used to explain Weber's law of the direct proportionality of antagonistic substances. By the union of the two antagonistic salts with the protoplasm, a substance is formed which inhibits death or injury. Assuming that this compound is formed in a surface, the amount formed will be independent of variations in concentration in the solution, and

will depend only on the proportion which the antagonistic salts bear to one another. L. M. U.

The Penetration of Balanced Solutions and the Theory of Antagonism. W. J. V. OSTERHOUT (*Science*, 1916, [*N. S.*], **44**, 395—396).—Antagonism has been explained by assuming that antagonistic substances prevent each other from entering the cell, but this explanation is not satisfactory, as it has been shown that penetration does occur when a cell is in a balanced solution, although at a slower rate than when in an unbalanced solution. As a way out of the difficulty, the author suggests that the antagonistic substances affect certain life processes which consist of consecutive reactions of the type $A \longrightarrow M \longrightarrow B$ (see this vol., i, 434), where M is a substance which determines, not only the electrical resistance of the protoplasm, but also its permeability to salts. Provided, therefore, that the substances are present in proportions which do not inhibit the life process, a certain amount of penetration may be expected to occur. L. M. U.

Permeability. IV. The Action of Various Organic Substances on the Permeability of the Plant Cell, and its Bearing on Czapek's Theory of the Plasma Membrane. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1917, **31**, 47—76).—Disks of potato tissue were immersed in solutions of various organic substances (alcohols, acetone, chloroform, ether, chloral hydrate, urethane, aniline, pyridine), and the effect of these substances on the permeability of the plasma membrane was determined by measuring the rate of exosmosis; the rate of exosmosis in its turn was measured by the electrical conductivity of the solution. It was found that in all cases the rate of exosmosis increased with the concentration of the solution employed, but equimolecular solutions of the different substances did not bring about the same degree of exosmosis; in the homologous series of the monohydric alcohols, the more complex the molecule the greater the exosmosis produced. No evidence was obtained of the existence for any solution of a critical concentration below which the exosmosis of electrolytes would not take place. The authors show that the rate of exosmosis produced by a solution cannot be a function of its surface tension alone, also that other assumptions used by Czapek in formulating his theory of the plasma membrane are untenable. From the ordinary laws of mass action, they deduce a mathematical expression connecting time and exosmosis, and the curve representing this equation is of the same form as those obtained from the actual experimental figures. L. M. U.

Permeability and Viscosity. W. J. V. OSTERHOUT (*Science*, 1916, [*N.S.*], **43**, 857—859).—It has been suggested recently that the permeability of the surface layer of protoplasm is determined by its viscosity, which in turn depends on its colloidal condition. Increased permeability may be produced by decreased viscosity and vice versa, but in the second case if the increased viscosity

goes beyond a certain point, a change occurs in the degree of intimacy between disperse phases and solvent with a sudden increase in permeability. The author applies this hypothesis to the results he obtained when determining the permeability and the electrical resistance of *Laminaria*, but finds that in several instances the theoretical deductions do not agree with the facts actually observed. L. M. U.

The Physiological Significance of Calcium in Plants. T. ROBERT (*Rev. gén. Sci.*, 1917, **28**, 101—108; from *Physiol. Abstr.*, 1917, **2**, 192—193).—Largely a review of the theories in regard to the action of calcium in plants. Experiments of the author on *Penicillium glaucum* and *Aspergillus niger* led him to the conclusion that small quantities of calcium sulphate (up to 0·01%) do not accelerate growth; somewhat larger quantities (0·04%) produce a slight increase in weight, due to fixation of the metal as oxalate. Above 0·4% calcium is toxic. Contrary to Osterhout's opinion, calcium has no antagonistic action in cultures of fungi. G. B.

The Micellary Theory of Nägeli as a Working Hypothesis in the Investigation of Chemical and Physical Changes in Cotton Fibres, with Special Reference to the Processes of Dyeing. R. HALLER (*Kolloid Zeitsch.*, 1917, **20**, 127—145).—The chemical and physical properties of cotton fibres lead to the conclusion that the outer membrane consists of two structural elements which show but small differences under normal conditions. When the cellulose is transformed into hydrocellulose and oxycellulose, the two components are much more readily differentiated. The difference is shown in the behaviour towards chemical reagents and in the appearance under the ultra-microscope. The proof that two such structural elements are involved is said to afford evidence in support of Nägeli's micellary theory of the structure of vegetable membranes. The absorption of mordants and dyes by the penetration of these substances into the micellary interstices is dependent on the degree of dispersity of the particles. The power of penetration is limited to particles of diameter less than about 5 $\mu\mu$. In the case of mercerised fibres, the micellæ are more widely separated than in the original untreated fibres, and particles of larger size than those above referred to may accordingly be absorbed, with the result that the depth of colour is greater. H. M. D.

Pectin Substances. I. SVEN ODÉN (*Int. Zeitsch. phys.-chem. Biol.*, 1917, **3**, 71—82).—The author demonstrates the presence of insoluble, or almost insoluble, acid substances in various plant tissues by a method based on the change in the electrical conductivity of an aqueous suspension of the tissue which occurs on the addition of a small amount of ammonium hydroxide. The plant

tissue after washing is brought to a finely divided state by prolonged grinding with water, and is then freed from traces of electrolytes by repeated centrifugalisation with pure water. Equal amounts of ammonia are added to equal volumes of the aqueous suspension and of pure water respectively; and a greater increase in the electrical conductivity in the former than in the latter case indicates the presence in the plant tissue of acid pectin substances, which form readily dissociated ammonium salts. The addition of dilute hydrochloric acid to the filtered ammoniacal suspension yields a gelatinous precipitate of the insoluble acid pectin substance (compare Schryver and Haynes, this vol., i, 245).

The author claims that these pectin substances, besides acting as the binding material of plant tissues, constitute a means for regulating the content of hydrogen and hydroxyl ions in the circulating fluids in the tissues and maintaining the cell-contents in a slightly acid condition. They form a reserve of insoluble acid, which is nevertheless readily available for the neutralisation of any alkaline substance brought into contact with the cell. H. W. B.

The Form of Iodine in Marine Algæ. Y. OKUDA and T. ETO (*J. Coll. Agric. Imp. Univ., Tokyo*, 1916, **5**, 341—353; from *Physiol. Abstr.*, 1917, **2**, 195).—Various fresh algæ (*Ecklonia, Turbinaria, Sargassum*) were found to contain only a minute quantity of iodides. Nearly all the iodine is in organic combination. The greater part of the iodine is in a form soluble in water, strong alcohol, dilute alkalis, or acids. It is not a protein compound. Concentrated solutions of sulphuric acid and sodium hydroxide decompcse it completely. Decomposition is also brought about by micro-organisms, but there is no enzyme in the plant to effect this.

Old algæ contain more iodine than young plants, and those growing in the open sea more than plants of the same species in inland waters. The greater part of the iodine easily diffuses from dead algæ into fresh- or salt-water, so that drifted algæ are unsuitable for the preparation of iodine. G. B.

Chemical Investigation of the Substance of the Birch. GEORG GRASSER (*Collegium*, 1916, 445—452; from *Chem. Zentr.*, 1917, i, 413. Compare A., 1912, ii, 593).—Young beech leaves, without previous desiccation, were extracted with cold toluene and a resin, m. p. 62°, obtained, the properties of which were identical with those of the substance previously described (*loc. cit.*). Further investigations prove the presence of one ketonic and two carboxylic groups, one of which is free and the other esterified by the butyl radicle. The substance is therefore *n*-butyl hydrogen betularetinate, $CO_2H \cdot C_{34}H_{60}O \cdot CO_2 \cdot C_4H_9$. The free acid must therefore have the formula $C_{36}H_{62}O_5$, whereas Kosmann (*J. Pharm. Chim.*, 1854, [iii], **26**, 197) gives $C_{36}H_{66}O_5$. It forms a reddish-yellow, transparent, brittle resin, readily soluble in alcoholic sodium hydroxide solution and the usual organic solvents, sparingly so in carbon tetrachloride. H. W.

Some Chemical Constituents of Green Plants. VIII. Detection of Formaldehyde in Plants. IX. Some Non-volatile, Water-soluble Constituents of the Leaves of the Edible Chestnut. T. CURTIUS and H. FRANZEN (*Sitz. Heidelberger Akad. Wiss. Math.-Nat. Kl. Abt.*, A., 1915, 8 pp.; *ibid.*, 1916, 18 pp.; from *Physiol. Abstr.*, 1917, **2**, 194—195).—VIII. The authors correct their previous view that formaldehyde can be demonstrated by steam distillation of green leaves, and oxidation of the distillate with silver oxide, yielding formic acid. They now hold with Fincke that formaldehyde is absent, and that the formic acid was probably derived from methyl alcohol, which they find is oxidised to this acid by silver oxide. IX. The authors obtained, after purification with lead acetate, a greyish-brown, amorphous, pectin-like substance, a tannin, and *i*-inositol. G. B.

Fucose or Fucosan in Fucus virsoides. E. VOTOČEK and B. RÖHLICH (*Zeitsch. Zuckerind. Böhm.*, 1916, **41**, 2—3).—*Fucus virsoides* from the coast at Abbazia, on the Gulf of Quarnero, was soaked first in water and then in 3% hydrochloric acid solution, the latter being removed by washing, and the purified seaweed then hydrolysed with 3% sulphuric acid solution. The resultant solution contained no galactose and little pentose, but a large proportion of fucose. T. H. P.

Methyl Nonyl Ketone from Palm Kernel Oil. ARTHUR HENRY SALWAY (T., 1917, **111**, 407—410).—Before being employed in the production of foods, many vegetable oils have to be submitted to a process of steam distillation in order to remove small quantities of volatile substances, chiefly neutral oils, which are detrimental to the taste and odour of the articles. In the case of palm kernel oil, it is now reported that the chief obnoxious constituent is methyl nonyl ketone, of which there is about 0·1% in the crude oil. This ketone is also found in cocoanut oil, but methyl heptyl ketone and methyl undecyl ketone are present as well (compare Haller and Lassieur, A., 1910, i, 808). J. C. W.

The Proteolytic Enzymes of Pinguicula vulgaris. K. G. DERNBY (*Biochem. Zeitsch.*, 1917, **80**, 152—158).—The dialysed expressed juice of *Pinguicula vulgaris* does not possess the property of thickening milk; it causes, however, a partial scission of milk caseinogen and of Witte's peptone when the reaction is neutral or faintly alkaline. The proteoclastic ferment causing the action is in many respects similar to trypsinogen, and the optimal hydrion concentration for its activity is about $p_H=8$. The juice contains no ereptic ferment (no action on glycylglycine), and no peptic ferment. S. B. S.

β-Galactosidase in the Vegetable Kingdom. MOUGNE (*J. Pharm. Chim.*, 1917, [vii], **15**, 339—345).—β-Galactosidase was found to be present in the kernels of plums, peaches, apricots, and

cherries, in the seeds of apples, in the fresh leaves of the cherry laurel, of horse-radish and of aucuba, and in the seeds of *Sinapis alba* and *nigra*. Negative results were obtained with fresh kephir and *Aspergillus niger*. W. G.

The Biochemistry of Plants. A. STUTZER (*Biochem. Zeitsch.*, 1917, **80**, 143—151).—Attention is directed to the fact that certain plant diseases are apt to appear in soils of which the reaction is alkaline, and experiment with a mildew on roses indicates that the disease will disappear if the plant is transferred to a more favourable soil. An account is given by the author of the method for determining the acidity or alkalinity. The soil extract is treated with solutions of potassium iodide and iodate. In the presence of free acids, the reaction $HIO_3 + 5HI = 3I_2 + 3H_2O$ takes place, and the iodine set free is titrated with thiosulphate. In the case of alkaline soils, the extract is treated with standard acid, the titre of which against thiosulphate is known; the diminution of this titre gives the amount of alkali. Variations in the amount of acid and alkali are, however, found in the same sample of the soil, which depend on the ratio of the amount of water used for extraction to the amount of soil. S. B. S.

Isolation of Stachydrin from Lucerne Hay. H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxvii; *J. Biol. Chem.*, 1917, **29**).—The author has isolated *l*-stachydrin in the pure form, and as the hydrochloride, from the phosphotungstic acid fraction of the water-soluble constituents of lucerne hay. H. W. B.

Soil Solution. J. P. VAN ZYL (*J. Landw.*, 1916, **64**, 201—275). —Various methods of obtaining representative soil solutions were compared, and it was found that extraction by pressure gave the best results. Using this method, the soil from a particular field was studied in detail and samples were taken from a limed and from a dunged plot in summer and in winter. These were subjected to pressure and the solutions obtained were analysed; the concentration of the solutions varied according to both the manurial treatment and the season of the year, but the percentage composition of the ash remained constant, thus lending support to the Cameron–Whitney theory of soil solution.

The author points out that in order to get a true knowledge of the physical structure of a soil, its mechanical analysis should be carried out in its own soil solution. Comparative sedimentation tests were made, using distilled water and soil solution; when soil solution was employed the liquid cleared much more quickly, but fifteen washings only removed 2% of the clay; on the other hand, when distilled water was used, deflocculation was more complete and fifteen washings removed all the clay from the soil. Two series of mechanical analyses were then undertaken on the soil samples mentioned above (that is, limed and dunged plots in summer and winter); in one case distilled water was used and in the other soil solution. The results again showed evidence of the flocculating

action of the soil solution, so much so that the separation of the three finest fractions from one another was not attempted. These groups of three fractions (0·006 to 0·0005 mm.) were afterwards treated with distilled water and complete separation effected. It was found that the number of washings required for the operation varied from 80 to 120, was higher on the dunged plot than on the limed plot, and higher in winter than in summer. L. M. U.

Relation between Indications of Several Lime-requirement Methods and the Soil's Content of Bases. C. J. SCHOLLENBERGER (*Soil Sci.*, 1917, **3**, 279—288).—Two soils were extracted with hydrochloric acid of various concentrations ranging from $N/100$ to $N/1$, and the free acid in the extracts was estimated by titration with $N/10$-sodium hydroxide. From the results, the amount of bases removed from the soils in each case was calculated. When these extracted bases were plotted against the strength of the acid used, the curve rose sharply up to a certain point and then much more slowly; it would appear that all the more easily soluble bases in the soil were dissolved by $N/5$-acid.

The residues from the extraction were then tested for lime requirement by the Hopkins, the Hutchinson-McLennan, and the vacuum methods, and it was found that the last gave results which corresponded best with the amount of base extracted.

The author suggests that the "total base-absorbing capacity" of a soil may be represented by adding the lime requirement as determined by the vacuum method to the amount of base extracted by $N/5$-acid, and that the bases extracted by $N/5$-acid may be taken as that part of the "base-absorbing capacity" which is already "satisfied." In this way, an expression can be obtained of the percentage of the total base-absorbing capacity or of the lime requirement which is still unsatisfied, and this may be used as a means of comparing the acidity or alkalinity of different soils. A series of pot cultures carried out to test this theory showed that the two neutral soils had more than 75% and the three alkaline soils 90% of their total base-absorbing capacity satisfied, whilst with all the acid soils the percentage was lower. L. M. U.

Organic Chemistry.

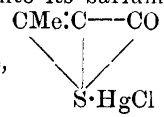
Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 100450, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 614).—In the preparation of acetic anhydride by the action of sulphur chlorides on sodium acetate, the evolution of sulphur dioxide and formation of chlorinated by-products may be avoided by: (*a*) using the reagents in the proportion of 6 atoms of chlorine to 8 acetyl groups; (*b*) employing a diluent such as acetic anhydride; (*c*) maintaining the temperature below 10—15°, and, preferably, below 0° until all the sulphur chloride has been added. Sulphur may be removed from the product by heating it with compounds of metals which form sulphides in the presence of acetic acid (such as the oxides or acetates of lead and copper), or it may be oxidised to sulphuric acid by permanganate, nitric acid, or nitrates. Thus, a mixture of dry powdered sodium acetate (720 kilos.) and acetic anhydride (600 kilos.) is cooled below 0° and sulphur dichloride (306 kilos.) is gradually introduced, the temperature being maintained at about 0° and the mixture being continually stirred. Stirring is continued for some time after the addition of sulphur dichloride is complete and the acetic anhydride is distilled off, preferably in a vacuum. The product is heated with a small quantity of copper oxide until free from sulphur. H. W.

Preparation of Acetic Anhydride. H. DREYFUS (Brit. Pat., 100452, addition to Brit. Pat., 100450, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 668).—In the process described in the original patent, the acetic anhydride should be distilled off in a vacuum at temperatures below 150°; otherwise, it is partly decomposed by the free sulphur with formation of acetic acid. H. W.

The Formation of Esters. D. MCINTOSH (*J. Amer. Chem. Soc.*, 1917, **39**, 1073—1074. Compare A., 1906, i, 481; Kendall and Booge, A., 1916, i, 707).—A very brief summary of work in progress. The freezing-point curves of systems such as methyl alcohol–acetic acid show no indication of the formation of compounds, but methyl or ethyl alcohol forms compounds with strong acids such as hydrobromic acid (compare Baume, A., 1912, ii, 329). Similar compounds are formed by acetic acid or its esters. Equimolecular mixtures of acetic acid and the alcohols apparently yield compounds with hydrobromic acid. At low temperatures there is no indication of ester formation. W. G.

Synthesis of αβ-Thiocrotonic Acid. PRAFULLA CHANDRA RÂY and MANIK LAL DEY (T., 1917, **111**, 510—512).—A solution of molecular proportions of thioacetamide and monochloroacetic acid in acetone gradually deposited ammonium chloride with simultaneous formation of *αβ-thiocrotonic acid*, $\begin{matrix}CMe\\ |\\ S\text{---}\end{matrix}\!\!>C\cdot CO_2H$, which

was further converted into its barium, lead, and silver salts and a chloromercuri-derivative,



The acid was reduced by hydriodic acid to β-iodo-αβ-thiobutyric acid, $\begin{matrix}\text{CMeI}\\ \text{S}\end{matrix}\!\!>\!\text{CH}\cdot\text{CO}_2\text{H}$, which was isolated in the form of its silver salt. In accordance with the general rule, αβ-thiocrotonic acid possesses a higher dissociation constant than its sulphur-free analogue crotonic acid.

For details the original should be consulted. D. F. T.

Incomplete Hydrogenation of Cotton-seed Oil. HUGH K. MOORE, G. A. RICHTER, and W. B. VAN ARSDEL (*J. Ind. Eng. Chem.*, 1917, **9**, 451—462).—An investigation of the changes in the amount, character, and chemical characteristics of the glycerides in oils during hydrogenation, and the changes in the properties of the oils themselves as regards saponification value, melting point, the response to the Halphen test, etc. The changes in the composition and the oil constants are expressed graphically, and the paper is illustrated with curves and diagrams. The conditions of hydrogenation, such as pressure, temperature, percentage of catalyst, and the degree of agitation were shown to affect the proportions of saturated glycerides, olein, and linolein in partially hydrogenised cotton-seed oil, and the effect of these variables on the velocity of hydrogenation was studied by means of iodine number-time curves. The increase in velocity is roughly proportional to the increase in pressure or amount of catalyst, whilst increase in temperature of 10° between 160° and 180° increases the rate by only about 20%. The change in the melting point of the oil and its fatty acids during hydrogenation was also followed by iodine number curves, and the latter was found to pass through a minimum before beginning to increase. The degree of hydrogenation necessary to destroy the response of cotton-seed oil to the Halphen test corresponds with a drop of about four units in the iodine number. Experiments on the influence of certain inorganic materials on the catalyst showed that whilst sodium chloride, nitrate, and sulphate, nickel chloride, and reduced iron had no effect, sodium sulphide, sulphur, chlorine, sulphur dioxide, hydrogen sulphide, or water vapour in the hydrogen destroyed the activity of the catalyst. G. F. M.

Preparation of Deoxycholic Acid. WILLIAM MAIR (*Biochem. J.*, 1917, **11**, 11—13. Compare Wieland and Sorge, A., 1916, i, 710).—Deoxycholic acid has a remarkably intense solvent action on pneumococci. It is prepared with maximum yield from ox bile by prolonged boiling with sodium hydroxide and subsequent neutralisation with hydrochloric acid. After filtration, the acid is thrown down by acetic acid and purified by several recrystallisations from 60% acetic acid. The yield of pure deoxycholic acid is about 10 grams from a litre of bile. H. W. B.

Synthesis of Hæmatic Acid and the Oxidation of Hæmatin. William Küster and Johannes Weller (*Zeitsch. physiol. Chem.*, 1917, **99**, 229—254. Compare A., 1914, i, 442).—A detailed description of work previously published.

Ethyl α-acetylglutarate, $C_{11}H_{18}O_5$, prepared from ethyl acetoacetate and ethyl iodopropionate by the action of sodium, is a colourless oil, b. p. 169—171°/22—25 mm.

Racemic *β-hydroxypentane-βγε-tricarboxylic acid*, $C_8H_{12}O_7$, crystallises with $1H_2O$ and has m. p. 108—110°.

The lactone of the above acid on heating yields, besides methylethylmaleic anhydride, a small amount of a crystalline substance which appears to be a *derivative* of *itaconic acid*, empirical formula, $C_7H_{10}O_4$, m. p. usually 179—180° (decomp.), but varies with rate of heating. The same compound is formed by heating hæmatic acid.

Varying yields of hydroxy-acids are obtained by oxidising hæmatin with various oxidising agents. H. W. B.

Compounds of Calcium Chloride and Acetone. Lancelot Salisbury Bagster (T., 1917, **111**, 494—497).—Calcium chloride combines with acetone to form two compounds, which, according to vapour pressure measurements, have the composition $CaCl_2,2C_3H_6O$ and $CaCl_2,C_3H_6O$ respectively. The dissociation pressures of the compounds have been determined at temperatures between 20° and 64°. H. M. D.

Preparation of Ketones. G. Schicht and A. Grün (D.R.-P., 295657; from *J. Soc. Chem. Ind.*, 1917, **36**, 569—570).—Ketones may be prepared by heating monocarboxylic acids of b. p. above 300° in the liquid state to temperatures not greatly exceeding 300° with small quantities of ketone-producing catalysts (finely-divided metals, oxides, silicates, or silicic acid). Mixtures of catalysts, or catalysts deposited on finely-divided carriers or on filtering material, may be employed. In consequence of the relatively low temperature of the reaction and the absence of energetic reagents, the yield is practically quantitative. Stearic acid yields stearone, $CO(C_{17}H_{35})_2$, m. p. 87°. Commercial stearin, m. p. 54°, gives a mixture of stearone, palmitone, and stearopalmitone, m. p. 75°.
H. W.

Preparation of Ketones. G. Schicht and A. Grün (D.R. P., 296677; addition to D.R.-P. 295657; from *J. Soc. Chem. Ind.*, 1917, **36**, 615. Compare preceding abstract).—Monocarboxylic acids of b. p. above 300° are heated in the liquid state in iron vessels without the addition of catalysts. Thus technically pure stearic acid, m. p. 68°, gives a quantitative yield of technically pure stearone, m. p. 84·6°, free from acid, when heated for three hours at 295°. It is not necessary to provide for the continuous removal of carbon dioxide and water as might be expected; the operation is preferably carried out in an autoclave. H. W.

The Preparation of Xylose. C. S. HUDSON and T. S. HARDING (*J. Amer. Chem. Soc.*, 1917, **39**, 1038—1040).—An 8—12% yield of xylose can be obtained from cotton-seed hulls by direct acid hydrolysis. The hulls are first left in contact with 2% ammonium hydroxide for twelve hours and then boiled with 7% sulphuric acid for two hours. The hulls are strained off and the liquid neutralised with calcium hydroxide. The calcium sulphate is filtered off, the filtrate decolorised with charcoal, and concentrated under reduced pressure. Alcohol is added, and the liquid, after filtration, is further concentrated to a syrup, from which by suitable treatment with alcohol the xylose is obtained in a crystalline form. W. G.

Sedoheptose, a New Sugar from Sedum spectabile. I. F. B. LA FORGE and C. S. HUDSON (*J. Biol. Chem.*, 1917, **30**, 61—77).—An aqueous extract of the leaves and stems of one of the stonecrops, *Sedum spectabile*, contains a non-fermentable, reducing sugar, *sedoheptose*, $C_7H_{14}O_7$, which has been obtained in the form of a dextro-rotatory syrup. When treated with phenylhydrazine, it yields a *phenylosazone*, $C_{19}H_{24}O_5N_4$, m. p. 197° (decomp.). The corresponding p-*bromophenylosazone*, $C_{19}H_{22}O_5N_4Br_2$, crystallises in bright yellow needles from methyl alcohol, m. p. 227—228° (decomp.). The *osone*, prepared in the usual way, does not crystallise readily, but its o-*phenylenediamine* derivative, $C_{13}H_{16}O_5N_2$, is deposited in long, white needles after the addition of a hot aqueous solution of *o*-phenylenediamine to the osone syrup. It crystallises with $\frac{1}{2}H_2O$ and melts at 163—165°.

By the reduction of a solution of the sugar from the plant extract with sodium amalgam, two heptahydric alcohols are produced. α-*Sedoheptitol*, $C_7H_{16}O_7$, has m. p. 151—152° and $[\alpha]_D^{20}$ +2·25°, and when dissolved in 50% sulphuric acid and treated with benzaldehyde it yields *tribenzylidene-α-sedoheptitol*, $C_{28}H_{28}O_7$, m. p. 199—200°. From the syrupy residue after the separation of α-sedoheptitol, a second benzaldehyde compound is isolated which is found to be *tribenzylidene-β-sedoheptitol*, $C_{28}H_{28}O_7$, crystallising from methyl ethyl ketone in tufts of flexible needles resembling asbestos, m. p. 272—275°. On hydrolysis, the free optically inactive *β-sedoheptitol*, $C_7H_{16}O_7$, is obtained, prisms, m. p. 127—128°.

On heating the plant extract with dilute acid, it loses about 80% of its reducing power towards Fehling's solution. When the extract which has been heated with acid is treated with benzaldehyde, a crystalline compound is obtained which proves to be the benzylidene derivative of a heptose which has lost one molecule of water. *Dibenzylideneanhydrosedoheptose*, $C_{21}H_{20}O_6$, is insoluble in most of the usual solvents, but crystallises from hot acetic anhydride in long white prisms, m. p. 245°. On hydrolysis, the crystalline anhydride is obtained. *Anhydrosedoheptose*, $C_7H_{12}O_6$, m. p. 155°, $[\alpha]_D^{20}$ −146·3° without mutarotation, does not reduce Fehling's solution, but on heating with dilute acid, it passes to the extent of about 20% into sedoheptose. Since boiling the original syrup containing sedoheptose with dilute acid diminishes the reducing power until it is about 20% of that originally ob-

served, it follows that mutual transformation of these two substances occurs in acid solution until equilibrium is established, when the solution contains 20% of sedoheptose and 80% of anhydrosedoheptose.

Sedoheptose is probably a ketose, because bromine does not oxidise it, and the two alcohols mentioned above result from its reduction. H. W. B.

Indirect Measurements of the Rotatory Powers of some α- and β-Forms of the Sugars by Means of Solubility Experiments. C. S. HUDSON and E. YANOVSKY (*J. Amer. Chem. Soc.*, 1917, **39**, 1013—1038).—In order to test the suggestion previously made by Hudson (compare A., 1909, i, 135) that the difference between the molecular rotations of the α- and β-forms of the sugars showing mutarotation is a constant quantity, the authors have determined the rotations of the unknown forms of the mutarotating sugars by the method previouslv described for lactose (compare Hudson, A., 1904, i, 974; Lowry, T., 1904, **85**, 1551). This depends on the measurement of the maximum rate of solution of the corresponding known isomeride or of its initial and final solubility. It is now shown that these mutarotating sugars have another common property, namely, a measurable maximum rate of solution, which is caused by the slow establishment in solution of equilibrium between the α- and β-forms. Sugars showing no mutarotation do not give this maximum rate of solution. The values obtained for the specific rotations of the α- and β-forms in water at 20° and the velocity coefficients of the mutarotation of the sugars examined are:

	Specific rotation in water.			Velocity coefficients of mutarotation.
Sugar	α-form.	Constant rotation.	β-form.	
d-Glucose	+113·4°	+52·2°	+19·0°	0·0065
d-Galactose	+144·0	+80·5	+52·0	0·0102
d-Mannose	+34·0	+14·6	−17·0	0·0190
d-Fructose	−21·0	−92·0	−133·5	0·082
d-Xylose	+92·0	+19·0	−20·0	0·021
d-Lyxose	+5·5	−14·0	−36·0	0·065
d-Arabinose	−54·0	−105·0	−175·0	0·031
l-Rhamnose	−7·7	+8·9	+54·0	0·039
α-Glucoheptose	+45·0	−20·4	−28·4	0·0122
Lactose	+90·0	+55·3	+35·0	0·0046
Maltose	+168·0	+136·0	+118·0	0·0072
Melibiose	+179·0	+142·5	+124·0	0·0088
Cellose	+72·0	+35·0	+16·0	0·0047

The highest value previously recorded for the specific rotation of α-glucose is 110° (compare Hudson and Dale, this vol., i, 320), but the specimen prepared for this work had $[\alpha]_D^{20}$ +113·4° in water, +115·2° in 80% alcohol, and +121·5° in absolute methyl alcohol.

The results obtained show fairly constant differences between the molecular rotations of the α- and β-forms, except in the case of mannose, lyxose, and rhamnose. It is possible that the exceptional difference for these sugars may be dependent on a configuration

type, since the configurations of these three sugars are identical from the γ-carbon atom upwards.

The initial and final solubilities of most of the crystalline sugars in various strengths of alcohol are tabulated in the original.

W. G.

The Preparation of β-Glucose. A. W. MANGAM and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 965—968).—The authors find that Behrend's method for the preparation of β-glucose (compare A., 1911, i, 14) by crystallisation of α-glucose from pyridine is satisfactory. The product is best dried at 105° or in a vacuum desiccator over sulphuric acid.

W. G.

The Rotatory Powers of some New Derivatives of Gentiobiose. C. S. HUDSON and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1272—1277).—By a modification of Zemplén's process (A., 1913, i, 707), the authors have obtained a greatly increased yield of gentiobiose octa-acetate (m. p. 192—193°, $[\alpha]_D^{20} -5\cdot3°$) from commercial gentian root. This octa-acetate when heated in acetic anhydride containing a little zinc chloride undergoes transformation into an *isomeride*, m. p. 188—189°, $[\alpha]_D^{20} +52.3°$ (in chloroform). It has already been shown that the α- and β-octa-acetates of maltose, lactose, and cellose in each case differ in specific rotation by approximately 57°, and in accordance with this result Zemplén's octa-acetate must be regarded as the β-compound and the new isomeride as the α-compound.

β-Gentiobiose octa-acetate, by the action of an acetic acid solution of hydrogen bromide, was converted into the syrupy bromohepta-acetyl *compound*, which on treatment with silver carbonate in methyl alcoholic solution gave *β-hepta-acetylmethylgentiobioside*, $C_{12}H_{14}O_{10}Ac_7\cdot OMe$, m. p. 82°, $[\alpha]_D^{20} -18\cdot8°$ in chloroform, this rotatory power agreeing approximately with the value calculated from the molecular rotation of the acetylated gentiobiose chain and of the lactonyl carbon of the acetylated methyl glucosides. Hydrolysis of the last product with aqueous barium hydroxide yielded *β-methyl gentiobioside*, $C_{12}H_{21}O_{10}\cdot OMe$, m. p. 98°, $[\alpha]_D^{20} -36\cdot0°$ in water, this rotatory power also approximating to that expected from the values for the gentiobiose chain and the asymmetric lactonyl carbon atom of the methyl glucosides.

D. F. T.

Action of Formaldehyde on Lactose, Maltose, and Sucrose. A. HEIDUSCHKA and H. ZIRKEL (*Arch. Pharm.*, 1916, **254**, 456—487).—The observations recorded in the literature of the action of formaldehyde on different kinds of sugars are so contradictory that a further study of the subject appears desirable. The authors have examined the substances obtained from formaldehyde and lactose, maltose, or sucrose in aqueous solution. Formaldehyde and the biose yield products the compositions of which vary with the relative proportions of the sugar and formaldehyde used in the preparation, and any one product does not differ in essential chemical characteristics from any other product or from its com-

ponents. The products therefore are not to be regarded as definite chemical compounds. Products containing up to 39% of formaldehyde have been prepared; from products containing a higher percentage paraformaldehyde separates. Products containing a high percentage of formaldehyde yield products containing a lower percentage by evaporating their aqueous solution in a vacuum. The capacity to take up formaldehyde is different in the three bioses, being greatest in sucrose and least in maltose. The formaldehyde in the products can be estimated by the sulphite method and the sugar polarimetrically, the sum of the two percentages being 100.

Following the directions of Oppermann and Goehde (Brit. Pat., 6653 of 1897) and of Rosenberg (A., 1908, i, 320), the authors have been unable to obtain from lactose and formaldehyde substances having the compositions recorded by these investigators. The products lose all their formaldehyde at 190° and leave pure lactose. The products are soluble in alcohol. This is noteworthy since lactose is practically insoluble in this solvent. The authors now find, however, that lactose is more soluble in alcohol containing formaldehyde than in alcohol alone, and that the products mentioned above are more soluble in alcohol the greater is their formaldehyde content; from such solutions lactose is deposited almost quantitatively as the formaldehyde progressively reacts with the solvent.

Other properties of sugar and formaldehyde solutions, such as the density and the viscosity, have been examined, and the authors are of opinion that the products obtained from formaldehyde and a biose are solid solutions of formaldehyde in the sugar. Since the sugar takes up relatively more formaldehyde from dilute solutions of formaldehyde than from concentrated solutions, adsorption processes would appear to be operative were it not that van Bemmelen's adsorption formula ($C_w^n/C_\lambda = k$) is found not to hold.

C. S.

The Reaction between Starch and Formaldehyde, and the Diastatic Properties of Formaldehyde. GERTRUD WOKER (*Ber.*, 1917, **50**, 679—692. Compare this vol., i, 61).—Polemical. A reply to von Kaufmann (this vol., i, 251) and a criticism of his experiments. In this, and in her first communication, the writer continually refers to experiments conducted by her colleague, Maggi, the details of which are to be published in another place. Apparently, a knowledge of these would have prevented confused criticism, for, as the following summary indicates, formaldehyde does somewhat resemble diastase in its behaviour towards starch.

(1) The microscopic appearance of the attack on starch granules by diastase and formaldehyde is the same. If the preparations are stained with iodine, a mosaic of blue, violet, red, brown, and yellow granules, representing unchanged starch and various dextrins, is obtained in each case. (2) Formaldehyde and diastase both liquefy starch. (3) Solutions of starch with diastase or formaldehyde behave towards iodine like mixtures of starch and achroo- and erythro-dextrins. (4) On dialysing the mixture of

starch and formaldehyde, the residue reacts like a mixture of starch and dextrins, and the dialysate like a solution of lower dextrins, and even sugars, with formaldehyde. (5) The viscosity of a solution of starch and formaldehyde or diastase is lower than the mean viscosity of the constituents. (6) The freezing points of such mixtures are also lower than the mean. (7) Solutions of starch, glycogen, or dextrin and formaldehyde respond to the Moore-Heller reaction when sufficient alkali to destroy the formaldehyde is added, and they also give the typical caramel-like odour when treated with concentrated sulphuric acid. (8) Solutions of starch or dextrin and formaldehyde respond to Rubner's reaction if the formaldehyde is boiled away. (9) Mixtures of starch and formaldehyde have a greater reducing power towards Fehling's and Pavy's solutions than solutions containing the same amount of the aldehyde alone. J. C. W.

Compounds of Amino-acids and Ammonia. IX. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1917, **99**, 150—160. Compare A., 1916, i, 713).—Hydrolysis of iminodiacetamide with excess of sodium hydroxide yields iminodiacetic acid, which is isolated by means of its β-naphthalenesulphonyl derivative, already described (Bergell and Feigl, A., 1908, i, 396). The intermediate monoamide is obtained by subjecting iminodiacetamide to the action of the enzymes contained in the fresh liver of a mouse. The *β-naphthalenesulphonyl* derivative of the monoamide of iminodiacetic acid, $C_{10}H_7\cdot SO_2\cdot N(CH_2\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2H$, crystallises in rosettes of plates, m. p. 202—204° (decomp.).

Benzoyliminodiacetamide gives off one molecule of ammonia when boiled with weak alkali hydroxide, leaving the *monoamide* of benzoyliminodiacetic acid, $C_{11}H_{12}O_4N_2$, prismatic needles, m. p. 190—191°.

Sarcosine may be readily recognised and isolated from its solutions by means of its *β-naphthalenesulphonyl* derivative,

$$C_{10}H_7\cdot SO_2\cdot NMe\cdot CH_2\cdot CO_2H,$$

which is prepared in the usual way, and crystallises in long needles from alcohol, m. p. 169—171°.

Glycineamide reacts with chloroacetylglycineamide, forming a derivative of iminodiacetic acid, which on benzoylation gives *benzoyliminoacetamidoacetylglycineamide*,

$$COPh\cdot N(CH_2\cdot CO\cdot NH_2)\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

crystallising with $1H_2O$ in prisms from alcohol, m. p. 186—188°.

H. W. B.

The Constitution of Cyanamide. EMILE COLSON (T., 1917, **111**, 554—561).—The densities and refractive indices of cyanamide and diethylcyanamide have been determined at 48°. The molecular refractivities, calculated according to the Lorenz-Lorentz formula, are compared with the corresponding numbers obtained by Brühl for dipropylcyanamide, di*iso*amylcyanamide, and carbodipropylimide. The refractivity of the CN_2 group is obtained by subtracting from the above molecular refractivities the values of the refractivity of the contained hydrogen atoms or alkyl groups.

The refractivity of the CN_2 group in cyanamide, diethyl-, dipropyl-, and di*iso*amyl-cyanamide is thus found to be equal to about 8, whilst the refractivity of this group in carbodipropylimide is about 10. The structure of cyanamide is therefore in accordance with the formula $N:C\cdot NH_2$.

The data are also discussed in relation to the atomic refractive power of nitrogen in the cyanamides. H. M. D.

Formation of Guanidine from Thiocarbamide and from Cyanamide. ERNST SCHMIDT (*Arch. Pharm.*, 1916, **254**, 626—632).—Schenk has shown (A., 1911, i, 842; 1912, i, 685) that alkylated guanidines are obtained by desulphurising alkylated thiocarbamides in ammoniacal solution or in the presence of amines. The author now finds that, contrary to the old statement of Hofmann, dicyanodiamide is not the only product obtained when thiocarbamide in aqueous or aqueous-alcoholic ammonia solution is treated with yellow mercuric oxide for twenty-four hours at the ordinary temperature, guanidine also being produced, although not in large quantities. Cyanamide is first formed, which then mainly polymerises to dicyanodiamide, but also reacts with ammonia to some extent to form guanidine.

The same two changes occur when a solution of cyanamide, prepared by very faintly acidifying a solution of sodium cyanamide with 98% formic acid, is treated with mercuric oxide and aqueous ammonia as above, but the quantity of guanidine formed is somewhat larger and becomes considerably greater when the reaction is effected in a sealed tube at 100°. C. S.

The Crystal Form and Isomerism of some Ferrocyanides. GEORGE MACDONALD BENNETT (T., 1917, **111**, 490—494).—Crystallographic measurements of crystals of sodium ferrocyanide with an unusual development of faces are recorded and compared with previous data. Some of the crystals were found to be interpenetrative twins.

In connexion with this examination, the author prepared the α- and β-forms of sodium and potassium ferrocyanides and of the double salt formed by ammonium ferrocyanide with ammonium chloride (Briggs, T., 1911, **99**, 1019). Goniometric measurements of the two forms showed that in all three cases they are crystallographically identical. The differences in colour, density, and solubility of the two forms, which are adduced by Briggs in support of the view that the two forms are stereoisomeric, are attributed to traces of impurities and to errors in the measurement of the density and the solubility. The marked difference in the optical rotatory powers of alcoholic solutions supposed to contain *l*-menthylamine α- and β-ferrocyanides respectively remains unexplained, but it cannot be attributed to the existence of isomeric forms.

Other pairs of salts supposed to represent stereoisomeric forms are also crystallographically identical according to goniometric data. H. M. D.

Aromatic Hydrocarbons from the Thermal Decomposition of Natural Gas Condensate. J. E. ZANETTI and G. EGLOFF (*J. Ind. Eng. Chem.*, 1917, **9**, 474—478).—The tar obtained by the thermal decomposition of natural gas condensates at temperatures above 750° by the methods previously described (A., 1916, i, 625, 705) was further investigated. It gave on distillation to 170°, 9·7%; to 230°, 18·7%; to 270°, 11·4%; to 330°, 15·1%, and a residue, 30·1%. In addition, a further 1·0—1·5 c.c. of light oil per cubic foot of gas used was scrubbed out of the gaseous product. From the above fractions the following substances were isolated: benzene, toluene, naphthalene, acenaphthene, anthracene, phenanthrene, pyrene, and chrysene. The apparatus employed for the decomposition of the condensate is illustrated in the paper, and is essentially the same as that already described, with the addition of a Cottrell separator to precipitate the tar "fog." G. F. M.

Syntheses in the Indene Series. II. Synthesis of Diphenylindene. A. P. ORECHOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1702—1712).—The compound, m. p. 177—178°, previously regarded as 2:3-diphenylindene (A., 1914, i, 265), is not identical with the compound, m. p. 108—109°, similarly designated by Thiele and Ruggli (A., 1912, i, 866). These two compounds yield the same oxime when treated with amyl nitrite and sodium ethoxide, and both give 2:3-diphenyl-1-benzylideneindene when condensed with benzaldehyde in presence of potassium hydroxide. These results are explained on the assumption that the diphenylindene, m. p. 177—178°, is the 1:2-compound, which readily undergoes isomerisation into the 2:3-compound, m. p. 108—109°, under the influence of alkali. The remainder of this paper has been already published (*loc. cit.*). T. H. P.

Syntheses in the Indene Series. III. Synthesis of Phenylbenzylindene. A. P. ORECHOV and (MLLE.) R. GRINBERG (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1713—1724. Compare preceding abstract).—Dehydration of tribenzylcarbinol by treatment with acetyl chloride yields *β-phenyl-αα-dibenzylethylene* [*αγ-diphenyl-β-benzylidenepropane*], $CHPh:C(CH_2Ph)_2$, which forms an almost colourless, highly viscous liquid, b. p. 231—232°/11 mm., exhibits normal cryoscopic behaviour in benzene, and instantly decolorises a chloroform solution of bromine. *αβ-Dibromo-αγ-diphenyl-β-benzylpropane*,

$$CH_2Ph\cdot CBr(CH_2Ph)\cdot CHPhBr,$$

forms colourless needles, m. p. 127—128°, and has the normal molecular weight in freezing benzene. When heated in an oil-bath at 150—155°, this compound loses hydrogen bromide, giving *3-phenyl-2-benzylindene*, $C_6H_4{<}{\overset{CH_2}{\underset{CPh}{}}}{>}C\cdot CH_2Ph$, which crystallises in hard, colourless prisms, m. p. 92—93°, exhibits normal cryoscopic behaviour in benzene, and decolorises bromine in chloroform solution. Like indene derivatives in general, 3-phenyl-2-benzyl-

indene condenses with benzaldehyde in presence of alcoholic potassium hydroxide, yielding *3-phenyl-2-benzyl-1-benzylidene-indene*, $C_6H_4<\substack{C(:CHPh)\\ \text{———}CPh}>C\cdot CH_2Ph$, which forms small, golden-yellow needles, m. p. 174—175°.

In all the cases which have now been investigated of ring-formation with dibromo-derivatives of the general type

$$CH_2Ph\cdot CRBr\cdot CHR_1Br,$$

no hydrogen is attached to the second carbon atom of the propane chain, so that elimination as hydrogen bromide of the bromine atom united to the third carbon atom cannot occur otherwise than by ring-closure. The method is therefore now being extended to dibromo-compounds with which this condition does not hold, namely, $\alpha\beta$-dibromo-$\alpha\alpha\gamma$-triphenylpropane, $\alpha\beta$-dibromo-$\alpha\gamma$-diphenylpropane, and $\alpha\beta$-dibromo-γ-phenylpropane. These investigations are still incomplete, but the following compounds have been prepared.

$\alpha\alpha\gamma$-Triphenylpropan-α-ol, $CH_2Ph\cdot CH_2\cdot CPh_2\cdot OH$, obtained by the action of magnesium phenyl bromide on ethyl β-phenylpropionate, forms long, slender, colourless needles, m. p. 87—88°, and in concentrated sulphuric acid gives an intense orange-yellow solution rapidly becoming pale yellow.

$\alpha\alpha\gamma$-Triphenyl-Δ^{α}-propene, $CH_2Ph\cdot CH:CPh_2$, prepared by the dehydration of $\alpha\alpha\gamma$-triphenylpropan-α-ol by means of acetyl chloride or hydrogen chloride, forms a pale yellow, viscous oil, b. p. 229—230°/17 mm.

This olefinic hydrocarbon readily combines with two atoms of bromine. The dibromo-compound is a yellow, viscous oil which could not be crystallised; when boiled with acetic acid, it loses hydrogen bromide, with formation of the *monobromo*-derivative,

$$CPh_2:CBr\cdot CH_2Ph, \quad CPh_2Br\cdot CH:CHPh, \quad \text{or} \quad C_6H_4<\substack{CH_2\\ CPh_2}>CHBr,$$

which crystallises in very long, thin needles, m. p. 98—99°, and has the normal molecular weight in freezing benzene. The product obtained on heating the monobromo-derivative with alcoholic potassium hydroxide appears to be a mixture of the hydrocarbon, $C_{21}H_{16}$, with the compound $C_{21}H_{17}\cdot OH$ or $C_{21}H_{17}\cdot OEt$. T. H. P.

Separation of Secondary Arylamines from Primary Amines. JOHN THOMAS (T., 1917, **111**, 562—572).—Although primary aromatic amines react readily with ethyl oxalate, producing a mixture of a substituted oxamic ester and a substituted oxamide, secondary aromatic amines, for example, ethyl-*o*-toluidine, ethylaniline, and methylaniline, react very little under the same conditions. This difference in behaviour can therefore be applied to the separation of primary and secondary aromatic amines; if the b. p. of the ester is inconveniently close to that of the secondary amine, butyl oxalate can be used instead of ethyl oxalate.

For details of the effect of variation in the conditions of treatment see the original paper. D. F T.

Groups of Bases Obtained from Aromatic Amines and Formaldehyde. Roberto Lepetit and Carlo Maimeri (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 558—563. Compare this vol., i, 197, 198).—The authors have repeated Goldschmidt's work (A., 1898, i, 184) on the action of formaldehyde on *p*-phenetidine hydrochloride, the resultant products comprising the four bases: (1) methyl-*p*-phenetidine, b. p. 102—104°/4 mm.; (2) a base, m. p. 146—147°, obtained in small proportion and not investigated; (3) a base, $C_{18}H_{20}O_2N_2$, m. p. 140°, identical with that to which Goldschmidt ascribed the formula $C_{18}H_{22}O_2N_2$. The accuracy of the formulæ now suggested is shown by the compositions of the corresponding bases given under similar conditions by *p*-anisidine and *p*-toluidine, namely, $C_{16}H_{16}O_2N_2$ and $C_{16}H_{16}N_2$ respectively. (4) A base, forming a bitter, anæsthetic hydrochloride, to be described later. T. H. P.

Chemical Composition of the Higher Fractions of Maple-wood Creosote. Ernest J. Pieper, S. F. Acree and C. J. Humphrey (*J. Ind. Eng. Chem.*, 1917, **9**, 462—465).—The fractional distillation of maplewood creosote gave 75% of wood creosote and 25% of pitch. Of the former, 14% boiled at 93—195°, 31% at 195—230°, and 55% at 230—280°. The lower fractions consisted mainly of guaiacol and creosol, whilst the various fractions of creosote oil above 195° on extraction with alkali gave 15—25% of neutral oil, the residue being phenols, the sodium salts of which separated out from the alkaline solution. From the mixed salts benzoyl derivatives and oxidation products were prepared, and the presence of pyrogallol dimethyl ether, methylpyrogallol dimethyl ether, and propylpyrogallol dimethyl ether in the original creosote fractions was thus established. These constituents are identical with those found in beechwood creosote, but differ in the amounts present. G. F. M.

Analogies between Derivatives of Oxygen and those of Nitrogen. II. A. Angeli (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 480—484. Compare A., 1910, ii, 844, 948; Diels and Paquin, A., 1913, i, 839).—The analogy between hydrogen peroxide, hydroxylamine, and hydrazine is also shown by quinol, *p*-aminophenol, and *p*-phenylenediamine. Thus, on oxidation, the former compounds yield respectively O:O, O:NH, and NH:NH, the last two of these being highly unstable and exhibiting a marked tendency to polymerise and decompose: $2NH{:}O \longrightarrow OH{\cdot}N{:}N{\cdot}OH \longrightarrow N_2O + H_2O$ and $2NH{:}NH \longrightarrow NH_2{\cdot}N{:}N{\cdot}NH_2 \longrightarrow N_3H + NH_3$. Similarly, oxidation of the above benzene derivatives gives *p*-benzoquinone, *p*-benzoquinoneimine, and *p*-benzoquinonedi-imine; further, *p*-benzoquinoneimine yields a polymeride of unknown constitution, and *o*-benzoquinonedi-imine readily furnishes *o*-azoaniline.

Dimethylamine yields nitrosoamine when treated with nitrous acid, and dimethylaniline behaves similarly. Nitroethane gives methylnitrolic acid and *p*-nitrotoluene yields *p*-nitrobenzaldoxime. The formation of formic acid from chloroform and alkali

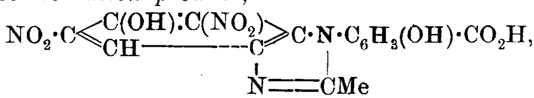
is analogous to Tiemann's synthesis of aromatic hydroxy-aldehydes. The transformation, $2CH_2Me\cdot NO_2 \longrightarrow NO_2\cdot CHMe\cdot CHMe\cdot NO_2$, corresponds with $2C_6H_4Me\cdot NO_2 \longrightarrow NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$.
T. H. P.

Preparation of Acyl Derivatives of 6-Amino-α-naphthol-3-sulphonic Acid. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 295767; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—Acyl derivatives of 6-amino-α-naphthol-3-sulphonic acid are prepared by condensing 3-hydroxy-β-naphthoic acid haloids, or the O-acetyl compounds, with 6-amino-α-naphthol-3-sulphonic acid. The products have strong affinity for cotton and silk. 3-Hydroxy-β-naphthoyl-6-amino-α-naphthol-3-sulphonic acid gives in alkaline solution the typical yellow colour of the 3-hydroxy-β-naphthoic acid arylamino-alkali salts. It combines with two molecules of diazo-compound and is absorbed by cotton from alkaline solutions and by silk from acetic acid solutions. Valuable colours, fast to washing, are obtained by treating the fabrics with diazo-compounds. H. W.

Condensation, under the Influence of Potassium Hydroxide, of *cyclo*Hexanol with *iso*Propyl Alcohol; Synthesis of *cyclo*Hexyl*iso*propyl Alcohol. MARCEL GUERBET (*Compt. rend.*, 1917, **164**, 952—954).—*cyclo*Hexanol and *iso*propyl alcohol, when heated in sealed tubes at 220° for twenty-four hours in the presence of anhydrous potassium hydroxide, undergo condensation, giving γ-cyclo*hexyl*iso*propyl alcohol*, $C_6H_{11}\cdot CH_2\cdot CHMe\cdot OH$, a colourless alcohol, b. p. 204—205°/764 mm. (corr.); D^0 0·9203, which forms an *acetate*, b. p. 213—214°/763 mm. (corr.), and a *phenylcarbamate*, prismatic needles, m. p. 124—125°. The alcohol when oxidised with chromic acid yields cyclo*hexylacetone* [cyclo*hexylmethyl methyl ketone*], b. p. 194—195°/761 mm. (corr.); D^0 0·9350, giving a crystalline *compound* with sodium hydrogen sulphite, and a *semicarbazone*, m. p. 199—200°. On further oxidation, the ketone gives acetic and *cyclo*hexanecarboxylic acids. W. G.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. I. 5-Aminosalicylic Acid and Related Compounds. RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (T., 1917, **111**, 533—546).—A preliminary investigation of 5-aminosalicylic acid and its derivatives with a view to the later production of derived quinone–ammonium compounds containing an asymmetric nitrogen atom.

5-Aminosalicylic acid resisted attempts at methylation, but was convertible into 5-*dibenzylaminosalicylic acid*, $C_{21}H_{19}O_3N$, which on subsequent methylation yielded 2-*carboxy*-4-*dibenzylmethylammonium*-1-*benzoquinone*, $O\colon C_6H_3(CO_2H)\colon NMe(C_7H_7)_2$. It reacted readily with 2 : 3 : 6-trinitro-4-acetylaminophenol, giving an iminazole *condensation product*,



and by diazotisation and subsequent coupling with β-naphthol was converted into 4-*hydroxy*-3-*carboxybenzeneazo*-β-*naphthol*,

$$OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H.$$

5-Nitro-3-aminosalicylic acid, obtained by reduction of the dinitrosalicylic acid, was converted through its *diazo-oxide* into 3-*chloro*-5-*nitrosalicylic acid*, 3-*chloro*-5-*aminosalicylic acid*, 3-*bromo*-5-*nitrosalicylic acid*, 3-bromo-5-aminosalicylic acid, and 5-*nitro*-3-*cyanosalicylic acid*. In addition to the preparation of various acetyl derivatives of these compounds there is described the production of the *benzyl* compound, $C_{14}H_{12}O_3NCl$, and of the *diazo-oxide*, $C_7H_3O_3N_2Cl$, derived from 3-chloro-5-aminosalicylic acid.

Experimental details will be found in the original. D. F. T.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. II. Nitrated Hydroxydiphenylamines. RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (T., 1917, **111**, 546—550. Compare preceding abstract).—2 : 4-Dinitro-4′-hydroxydiphenylamine was convertible into a monoacetyl and a diacetyl derivative, the former on nitration giving 2 : 4 : ?-*trinitro*-4′-*hydroxyacetyldiphenylamine*,

$$C_{14}H_{10}O_8N_4,$$

whilst the latter was less readily nitrated and yielded 2 : 4 : ? : ?-tetranitro-4′-hydroxyacetyldiphenylamine.

Other substances prepared were 2 : 4-*dinitro*-4′-*hydroxydiphenylmethylamine*, $OH\cdot C_6H_4\cdot NMe\cdot C_6H_3(NO_2)_2$, by the condensation of 4-chloro-1 : 3-dinitrobenzene with *p*-methylaminophenol; 2 : 4 : 6 : 3′ : 5′-*pentanitro*-4′-*hydroxydiphenylamine*, $C_{12}H_6O_{11}N_6$, by the condensation of picryl chloride with *iso*picramic acid; and a *substance*, $C_{12}H_8O_7N_4$, by the action of nitric acid on 2 : 4 : 6-trinitro-4′-hydroxydiphenylamine in acetic acid.

Attempts to alkylate or benzylate these nitrated hydroxydiphenylamines gave discouraging results.

For experimental details see the original. D. F. T.

Attempts to Prepare Asymmetric Quinquevalent Nitrogen Compounds. III. Hydroxyphenylglycine. RAPHAEL MELDOLA, HENRY STENNETT FOSTER, and RAINALD BRIGHTMAN (T., 1917, **111**, 551—553. Compare preceding abstracts).—A record of several fruitless attempts to prepare asymmetric quinone–ammonium compounds of the type $O:C_6H_4:NMe(C_7H_7)\cdot C_3H_5$ from hydroxyphenylglycine or its derivatives. In the course of the experiments *p*-*nitrobenzylisopicramic acid*, $C_{13}H_{10}O_7N_4$, was obtained from *iso*picramic acid and *p*-nitrobenzyl chloride.

For experimental details the original should be consulted.

D. F. T.

Preparation of a Bromo-derivative of *p*-Aminophenyl Salicylate. I. ABELIN, BERNE and S. LICHTENSTEIN-ROSENBLAT (D.R.-P., 297243, addition to D.R.-P., 291878; from *J. Soc. Chem. Ind.*, 1917, **36**, 668. Compare A., 1916, i, 645).—*p*-Aminophenyl salicylate is treated with an α-bromodiethylacetyl haloid instead

of an *α*-bromo*iso*valeryl haloid, as in the original patent. The new product has a stronger sedative, anti-rheumatic, and soporific action, and is tasteless. H. W.

Cyano-carbethoxy-3 : 3-dimethyl*cyclo*pentanone [Ethyl 2-Cyano-1 : 1-dimethyl*cyclo*pentane-3-one-2-carboxylate]. W. A. NOYES and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1917, **39**, 1267—1271).—A further examination of the chemical properties of ethyl 2-cyano-1 : 1-dimethyl*cyclo*pentane-3-one-2-carboxylate (Noyes, A., 1899, i, 929). The *oxime* of this ester, m. p. 108—110° (Hewes, *Thesis*, Illinois, 1914), when heated with dilute sodium hydroxide solution is converted into 2-*cyano*-1 : 1-*dimethyl*cyclo*pentan-3-oxime-2-carboxylic acid*, $OH\cdot N:C_7H_{10}(CN)\cdot CO_2H$, m. p. 142—143° (decomp.), which, when carefully heated, loses carbon dioxide with formation of 2-*cyano*-1 : 1-*dimethyl*cyclo*pentane-3-oxime*, $OH\cdot N:C_7H_{11}\cdot CN$, m. p. 127—128°. Hydrolysis of this substance or of its parent carboxylic acid with hydrochloric acid yielded carbon dioxide, ammonia, and presumably 1 : 1-dimethyl*cyclo*pentan-3-one (Blanc, A., 1908, i, 655), but the quantity was insufficient for definite identification. D. F. T.

Syntheses in the Naphthalene Series. OLIVER KAMM, H. B. MCCLUGAGE, and A. W. LANDSTROM (*J. Amer. Chem. Soc.*, 1917, **39**, 1242—1248).—A search for a more convenient preparation and an independent proof of the structure of 1 : 4-ethoxynaphthoic acid (Gattermann, A., 1888, 575).

4-Ethoxy-*α*-naphthyl methyl ketone, prepared by the action of acetyl chloride on a carbon disulphide solution of *α*-ethoxynaphthalene in the presence of aluminium chloride, was oxidised with alkaline permanganate solution, with formation of *α-ethoxynaphthoylformic* [*α-ethoxynaphthylglyoxylic*] *acid*,

$$OEt\cdot C_{10}H_6\cdot CO\cdot CO_2H,$$

m. p. 162°, and 1 : 4-ethoxynaphthoic acid, m. p. 217°. This acid was also obtained by oxidation of 1 : 4-ethoxynaphthaldehyde with alkaline permanganate. Reduction with sodium amalgam in hot alkaline solution converted the ethoxynaphthoic acid into 1 : 2 : 3 : 4-tetrahydro-1-naphthoic acid, the 2 : 3-dihydro-1-naphthoic acid and 1 : 2-dihydro-1-naphthoic acid being successive intermediate products. These results supply a complete demonstration of the structure of the 1 : 4-ethoxynaphthoic acid. D. F. T.

Studies in Identification. IV. Identification of Alcohols. E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1249—1255).—It has recently been shown that *p*-nitrobenzyl bromide reacts readily with the sodium salt of an acid to form an ester which, as a general rule, is crystalline (Reid, this vol., i, 333). By heating phthalic anhydride with an alcohol, the corresponding alkyl hydrogen phthalate is obtainable, primary alcohols reacting readily at 100°, whilst secondary alcohols need a temperature above 120°; the sodium salt derived from the acid ester is then convertible by the action of *p*-nitrobenzyl bromide into the corresponding alkyl

p-nitrobenzyl phthalate. The following mixed esters were obtained: p-*nitrobenzyl methyl phthalate*, m. p. 105·7°; p-*nitrobenzyl ethyl phthalate*, m. p. 80°; p-*nitrobenzyl propyl phthalate*, m. p. 53·0°; p-*nitrobenzyl* iso*propyl phthalate*, m. p. 74·0°; p-*nitrobenzyl allyl phthalate*, m. p. 61·5°; p-*nitrobenzyl* n-*butyl phthalate*, m. p. 62·0°; p-*nitrobenzyl* n-*octyl phthalate*, m. p. 41·0°; *benzyl* p-*nitrobenzyl phthalate*, m. p. 83·0°; p-*nitrobenzyl phenylethyl phthalate*, m. p. 84·3°; *bornyl* p-*nitrobenzyl phthalate*, m. p. 100°; iso*bornyl* p-*nitrobenzyl phthalate*, m. p. 87°. The corresponding products derived from *iso*butyl, *iso*amyl, and cinnamyl alcohols, and from menthol and geraniol, were uncrystallisable oils.

D. F. T.

The Phenylsuccinic Acid Series. IV. *l*-Menthyl Esters of the Diphenylsuccinic Acids. H. WREN and CHARLES JAMES STILL (T., 1917, **111**, 513—533; see also T., 1915, **107**, 447, 1454).—It has already been shown that aqueous-alcoholic potassium hydroxide converts ethyl *meso*diphenylsuccinate into a mixture of the potassium salts of *r*- and *meso*-diphenylsuccinic acids; the menthyl ester therefore promised to be of additional interest in view of the possibility that in its hydrolysis the dextro- and lævo-isomerides formed by the transformation of the *meso*-compound might not be produced in equimolecular proportion. The *l*-menthyl esters of diphenylsuccinic acid, however, proved too resistant to the action of alkali for the observation of this effect, even if it existed.

The diphenylsuccinic acids are not readily esterified by menthol. A mixture of *l*-diphenylsuccinic acid with excess of menthol at 115—120° in a current of hydrogen chloride yields a mixture of the *l*-menthyl hydrogen and di-*l*-menthyl esters. Under similar conditions, *d*-diphenylsuccinic acid gives *l*-menthyl hydrogen *d*-diphenylsuccinate as the only isolable product, and although a variety of methods was tried for the further conversion of this into the corresponding di-*l*-menthyl ester, the desired result was not attained. The racemic acid reacts with *l*-menthol under conditions similar to the preceding, giving rise to di-*l*-menthyl *l*-diphenylsuccinate, *l*-menthyl hydrogen *l*-diphenylsuccinate, *l*-menthyl hydrogen *r*-diphenylsuccinate, and *l*-menthyl hydrogen *d*-diphenylsuccinate. In this case the probable course of the change is the initial formation of *r*-diphenylsuccinic anhydride, which is subsequently converted into a mixture of the *l*-menthyl hydrogen esters of the *d*- and *l*-stereoisomeric acids; the *l*-menthyl hydrogen *l*-diphenylsuccinate, however, undergoes further esterification far more rapidly than the corresponding ester of the *d*-acid, so that the only isolable normal ester is that of the *l*-acid; the proportion of the acid esters of the *d*- and *l*-acids in the final mixture is disturbed by a partial resolution during the ethereal extraction, the potassium *l*-menthyl *d*-diphenylsuccinate being much more soluble than the corresponding *l*-diphenylsuccinate.

Di-*l*-menthyl *meso*diphenylsuccinate was prepared by heating the *meso*-acid with menthol at 150° in a current of hydrogen chloride, whilst the corresponding *r*-diphenylsuccinate was

obtained by the combination of equal quantities of the *d*- and *l*-diphenylsuccinates in acetone solution.

By the action of thionyl chloride on *l*-menthyl hydrogen *l*-diphenylsuccinate there was produced diphenylmaleic anhydride.

For experimental details reference must be made to the original. D. F. T.

Preparation of 1 : 5-Dihydroxynaphthalenedicarboxylic Acid. F. VON HEMMELMAYR (D.R.-P., 296501, addition to D.R.-P., 296035; from *J. Soc. Chem. Ind.*, 1917, **36**, 590).—Solid hydrogen carbonates are allowed to act on 1 : 5-dihydroxynaphthalene in presence of an indifferent solvent or medium, such as trichlorobenzene or nitrobenzene. H. W.

Lichens and their Characteristic Constituents. XV. O. HESSE (*J. pr. Chem.*, 1916, [ii], **94**, 227—270).—*Evernia furfuracea*, var. *olivetorina*. Continuing his investigation of the constituents of this lichen (A., 1911, i, 208), the author has now isolated, in addition to atranorin (about 0·25%) and olivetoric acid (about 2%), very small quantities of two new acids, which he names olivoric acid and *apo*olivoric acid.

Olivoric acid, $C_{23}H_{28}O_8$, faintly yellow, crystalline powder, m. p. 115—116°, which is insoluble in boiling light petroleum, forms an amorphous, easily soluble *potassium* salt, and in alcoholic solution develops a bluish-violet coloration with ferric chloride and a red coloration with calcium hypochlorite. apo*Olivoric acid*, $C_{23}H_{26}O_7$, leaflets, m. p. 108—109°, is soluble in boiling light petroleum, and in alcoholic solution gives a bluish-violet and a blood-red coloration with ferric chloride and with calcium hypochlorite respectively; in the case of both acids, the latter coloration disappears on further addition of the reagent.

By treatment with acetic anhydride and anhydrous sodium acetate, finally at 80—90°, olivetoric acid yields a *diacetyl* derivative, $C_{21}H_{24}O_7Ac_2$, a colourless varnish which is neutral to litmus, and is converted by hot water into a *monoacetyl* derivative, $C_{21}H_{25}O_7Ac$, colourless needles, m. p. about 116°, which in alcoholic solution is acid to litmus.

When heated with water at 150°, olivetoric acid yields carbon dioxide, olivetrolic acid, which has the composition $C_{19}H_{28}O_4$, not $C_{24}H_{34}O_5$ as recorded by Rave (*Diss.*, 1908), and *olivetorinol*, $C_{19}H_{24}O_6$, colourless leaflets, m. p. 104°. Olivetrolic acid forms colourless leaflets containing $2H_2O$, m. p. 26·5°, or anhydrous needles, m. p. 90°.

Parmelia saxatilis, var. *retiruga*.—This lichen has been shown to contain atranorin, saxatic acid, and an acid which was called protocetraric acid (A., 1903, i, 702); a small quantity of usnetic acid has also been isolated. The so-called protocetraric acid is not identical with the acid of this name obtained from *Cetraria islandica*, and has been renamed *parmatic acid* (Zopf's saxatilic acid).

Parmelia saxatilis, var. *omphalodes* (*Parmelia omphalodes*, L.).

—A specimen of this lichen gathered in the Carpathian Mountains was found to contain atranorin, usnetic acid, and parmatic acid, the last in considerable quantity. Another sample, collected at Hochkelch, Upper Alsace, yielded usnetic acid, parmatic acid (4·75%), atranorin, and a *substance*, $C_{24}H_{24}O_7$, needles, m. p. 197°, which is a lactone of usnetic acid and appears to be identical with Knop's lobaric acid.

Pertusaria.—The constituents of this genus of lichens have been the subject of considerable dispute. The author is of opinion that the bitter variety grown on the beech contains, together with a little picrolichenin, salazinic acid as the only acid, whilst *Pertusaria* grown on the lime-tree contains no picrolichenin, but salazinic acid and a trace of a neutral, crystalline substance. Pure salazinic acid is tasteless, not bitter, as stated by Zopf. When heated with an excess of acetic anhydride at 90° for three hours, or at the b. p. for half an hour, salazinic acid yields *tetra-acetylsalazinic acid*, $C_{30}H_{20}O_{16}Ac_4$, colourless, crystalline meal, m. p. 211°, which is tasteless, and in alcoholic solution has an acid reaction, and does not give a coloration with a little ferric chloride. The elevation of the b. p. of an acetone solution of the acetyl derivative corresponds initially with this formula, but after long boiling the elevation is doubled. It seems, therefore, that tetra-acetylsalazinic acid is dimeric, the bimolecular β-form changing in solution into the monomeric α-form, $C_{15}H_{10}O_8Ac_2$ (compare Zopf, A., 1907, i, 218).

When salazinic acid is heated with anhydrous sodium acetate (1 part) and acetic anhydride (3 parts) at 90—100° for three hours, it yields *α-monoacetylsalazinic acid*, $C_{15}H_{11}O_8Ac$, colourless needles containing H_2O, m. p. about 120° (hydrated) or about 150° (anhydrous), which has a bitter taste, gives in alcoholic solution an acid reaction, and with a little ferric chloride a reddish-brown coloration, and is converted by warm aqueous sodium hydroxide into brick-red needles of the sodium salt of rubidic acid, $C_{14}H_{12}O_6$ (the author has formerly given to the acid the formula $C_{28}H_{24}O_{12}$, which would correspond with the bimolecular form).

Cetraria nivalis Ach.—This lichen contains *l*-usnic acid (1·8%) and a new *acid*, $C_{20}H_{26}O_6$, faintly brown powder, which is named *nivalic acid*. The latter develops a brownish-red coloration with ferric chloride in alcoholic solution.

After removal of the preceding constituents by ether, the remainder of the lichen yields to boiling water about 11% of carbohydrates, consisting as to about one-quarter of lichenin and as to about three-quarters of a new carbohydrate, which is named l-*lichenidin*. The lichenin, $C_6H_{10}O_5$, is a colourless powder, m. p. about 275° (decomp., becoming brown at about 260°), which is optically inactive, does not give a coloration with iodine in aqueous solution, and yields only dextrose by hydrolysis with 5% sulphuric acid. l-*Lichenidin*, $C_{12}H_{22}O_{11}$, a colourless powder, does not give a coloration with iodine and has $[\alpha]_D^{15}$ $-16·8°$ in aqueous solution ($c=2$) in the presence of borax (1 mol.); it yields only dextrose by hydrolysis with boiling 5% sulphuric acid.

Cetraria islandica.—Zopf states (Flechtenstoffe, 1907) that

proto-α-lichesteric acid is identical with protolichesteric acid, despite a difference of 3·5 in the percentage of carbon. The author has examined samples of the lichen from different sources yearly since 1907, and has always found proto-α-lichesteric acid, except in two samples, which yielded an acid having the composition of protolichesteric acid, although, judging by some of its derivatives, it may be proto-α-lichesteric acid mixed with some unknown impurity.

Proto-α-lichesteric acid, $C_{18}H_{30}O_5$, forms leaflets, m. p. 107—108°. By slow heating a lower m. p. is observed, even as low as 92°, owing to a change into other acids, particularly dilichesteric and α-lichesteric acids; the same two acids are formed when a concentrated solution of proto-α-lichesteric acid in chloroform, acetone, alcohol, ether, or benzene is heated above 45°. Proto-α-lichesteric acid is converted into α-lichesteric acid by acetic anhydride at 90—100°, into lichestronic acid by boiling 10% potassium hydroxide, and into this acid and lichestrone by boiling aqueous barium hydroxide.

α-Lichesteric acid and dilichesteric acid do not occur as such in *C. islandica*, but are formed from the proto-α-lichesteric acid under the conditions stated above.

The author is of opinion that Zopf's protolichesteric acid is not an individual substance, but consists essentially of proto-α-lichesteric acid. Several times he has isolated acids, the composition and properties of which accorded well with those of protolichesteric acid ($C_{18}H_{30}O_4$), but since under the conditions stated above they yielded α-lichesteric, dilichesteric, and lichestronic acids, they are probably impure proto-α-lichesteric acid.

Cetrarinin has now been isolated from *Lichen island. concis.* as a colourless, crystalline powder, m. p. 228°; in alcoholic solution it does not change blue litmus or give a coloration with a little ferric chloride.

Contrary to statements in recent publications, cetraric acid does not occur as such in *C. islandica*, but is produced when attempts are made to obtain the bitter-tasting acids of the lichen through the agency of alcohol. If potassium carbonate and acetone instead of alcohol are employed, potassium fumarate and potassium protocetrarate are obtained, whilst by the use of acetone alone fumarprotocetraric acid is extracted from the lichen.

The carbohydrates in *C. islandica*, which are soluble in boiling water, are stated in the literature to be lichenin and *iso*lichenin. The latter is now found to consist of *d*-lichenidin and lichenoin. d-*Lichenidin*, $C_{12}H_{22}O_{11}$, is a white powder which has m. p. 270—280° (decomp.; darkening at about 240°), $[\alpha]_D^{15}$ +15·4° in water ($c = 2$) in the presence of borax (1 mol.), does not give a coloration with iodine, and yields only dextrose by hydrolysis with boiling 5% sulphuric acid. *Lichenoin*, $C_{12}H_{20}O_{10},4H_2O$, is an elastic substance like caoutchouc, which is easily soluble in cold water, and develops a blue coloration with iodine. After being dried in the air it becomes hard and inelastic. An aqueous solution of the substance dried at 100° has $[\alpha]_D^{18}$ +202·7° ($c = 0·944$), does not give a precipitate with tannin and develops with iodine

a less intense blue coloration than does the air-dried material. The hydrolysis of lichenoin by 5% sulphuric acid is complete only after boiling for four hours, the products being dextrose and an optically inactive substance which is isolated as the *compound*, $2C_6H_{10}O_5,Ba(OH)_2,3H_2O$, a colourless, hygroscopic powder having a neutral reaction in aqueous solution.

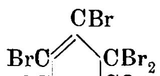
The carbohydrates in *C. islandica*, which are sparingly soluble or insoluble in hot water, yield after hydrolysis with sulphuric acid dextrose, a little *d*-galactose, and a trace of mannose.

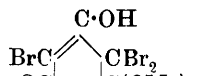
C. S.

Diazotisation of 4-Bromo-4′-aminobenzophenone in Alcoholic Solution. P. J. MONTAGNE (*Chem. Weekblad*, 1917, **14**, 526—529).—Diazotisation in alcoholic solution of 4-bromo-4′-aminobenzophenone produces a mixture of 4-bromobenzophenone, 4-bromo-4′-ethoxybenzophenone (m. p. 132°), and 4-bromo-4′-hydroxybenzophenone (m. p. 191°). The last compound can be separated from the mixture by means of alkali hydroxide, and the ethoxy-derivative partly by crystallisation from alcohol. The first compound is obtained free from the ethoxy-derivative by saponifying this with acetic acid and hydrobromic acid, and dissolving the hydroxy-compound formed by alkali hydroxide. The constitution of 4-bromo-4′-ethoxybenzophenone is established by its synthesis from 4-bromobenzoyl chloride, phenetole, aluminium chloride, and carbon disulphide.

A. J. W.

The Constitution of Xanthogallol. F. J. MOORE and RUTH M. THOMAS (*J. Amer. Chem. Soc.*, 1917, **39**, 974—1011).—A careful study of xanthogallol and its derivatives has led to the conclusion that the constitution assigned to this compound by Theurer (compare A., 1888, 1084) is incorrect, since it is not in accord with present molecular weight determinations or analyses, as the compound is now shown to contain no hydrogen. A much simpler cyclic formula (I) is suggested, based mainly on several series of reactions


(I.)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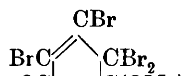
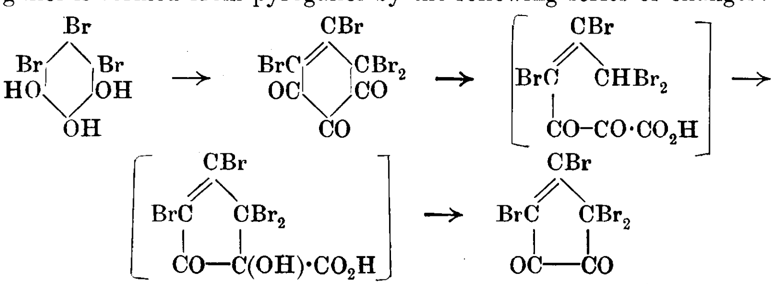

(III.)

leading to oxalic acid and brominated acetones. This formula also permits a simple interpretation of the reaction by which xanthogallol is formed from pyrogallol by the following series of changes:



Molecular weight determinations by the cryoscopic method give values ranging from 379—403, whereas the formula put forward by Stenhouse (compare this Journal, 1874, 586) and confirmed by Theurer requires 1436. For the hydrogen determinations, combustions were performed using 1 gram samples, to eliminate error due to moisture, and no hydrogen was found to be present. The new formula gives a good account for the composition and relationships of all of Theurer's derivatives and also of certain new ones. These are set out in detail in the original.

No less than three independent methods of decomposition of xanthogallol lead to oxalic acid or its derivatives, thus confirming the adjacent position of the carbonyl groups. Further, with *o*-phenylenediamine it gives a *quinoxaline* derivative,

$$C_5Br_4{:}N_2{:}C_6H_4,$$

m. p. 186—187°, free from oxygen. The aniline derivative of xanthogallol (*loc. cit.*) also gives a *quinoxaline* derivative, $NHPh{\cdot}C_5Br_3{<}^{N}_{N}{>}C_6H_4$, decomposing at 210°, and a similar *compound*, $C_5Br_3Cl{<}^{N}_{N}{>}C_6H_4$, m. p. 171—172°, is obtained from chloroxanthogallol.

When hydrogen chloride is passed into a solution of xanthogallol in methyl alcohol, the product is not chloroxanthogallol methyl acetal, but xanthogallol methyl acetal (formula III) with a certain amount of the chlorinated acetal. The latter acetal with alkali gives the methyl acetal of hydroxyxanthogallol (formula II), which with hydrochloric acid in methyl alcohol gives the *methyl ether* of this acetal, and not the compound,

$$C_6HBr_4Cl(OMe)_4,$$

as stated by Theurer. The position of the hydroxyl group in hydroxyxanthogallol, and thus of the reactive bromine atom in xanthogallol, is confirmed by the fact that hydroxyxanthogallol is decomposed by bromine water, giving oxalic acid and pentabromoacetone. The behaviour of hydroxyxanthogallol towards aniline and *p*-toluidne is different from that given by Theurer. If *p*-toluidine is added in insufficient amount to the hydroxy-compound in alcohol, a *compound*, m. p. 89—90°, is obtained, which is the *p*-toluidine salt. When this is crystallised from alcohol or dilute acetic acid, a hydrated product, m. p. 102—104°, is obtained which when dried gives a *compound*, m. p. 147—148°. In the formation of these last two compounds the toluidine molecule must have migrated to one of the carbonyl groups, since with aniline they both give oxanilide-*p*-toluidide. Similarly with aniline, the *aniline* salt, m. p. 70°, is obtained, which is converted into a *compound*, m. p. 148—149°, which with aniline gives oxanilide, and with *p*-toluidine, oxanilide-*p*-toluidide.

The acid, m. p. 124° mentioned by Theurer as obtained from xanthogallol by the action of sodium hydroxide is best prepared from hydroxyxanthogallol and alkali, and is now named *xanthotonic acid*, m. p. 110—115°. and assigned the constitution $CHBr{:}C(OH){\cdot}CBr_2{\cdot}CO{\cdot}CO_2H$. With bromine water in the cold it

gives pentabromoacetone, and with hydrochloric acid and potassium chlorate *chlorotribromoacetone*,

$$CHBr_2{\cdot}CO{\cdot}CHClBr,4H_2O,$$

m. p. 64—65°. W. G.

Action of γ-Diketones on Unsaturated Ketones. M. SCHOLTZ (*Arch. Pharm.*, 1916, **254**, 547—566, 625).—The reaction between acetylacetone and phenyl cinnamylidenemethyl ketone has been examined in the expectation that the conjugation of the double linkings of the latter would determine the course of the reaction. This expectation has not been confirmed.

When an alcoholic solution of phenyl cinnamylidenemethyl ketone (1 mol.) and acetylacetone (2 mols.) is boiled for three hours with 20% aqueous sodium hydroxide (2 mols.), two substances, $C_{20}H_{18}O$ and $C_{22}H_{24}O_4$, are produced in about equal quantities. The former, which alone is produced when the reaction is effected in absolute alcohol and sodium ethoxide is used instead of sodium hydroxide, is a neutral substance crystallising in colourless plates, m. p. 105°, which forms an *oxime*,

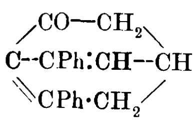
$$C_{20}H_{18}{:}NOH,$$

needles, m. p. 173°; *semicarbazone*, needles, m. p. 187°; *dibromide*, $C_{20}H_{18}OBr_2$, needles, m. p. 167°; *tribromide*,

$$C_{20}H_{17}OBr_3,$$

rhombic plates, m. p. 204° (by loss of hydrogen bromide from the initially formed tetrabromide); and *tetrachloride*, needles, m. p. 72—74°. From the researches of Michael (1887), Auwers (1891), and Knoevenagel (1894—1903) on this type of reaction, there can be no doubt that the substance $C_{20}H_{18}O$ is 1-*phenyl*-5-*styryl*-Δ^1-cyclo*hexen*-3-*one*, $CHPh{:}CH{\cdot}CH{<}^{CH_2{\cdot}CPh}_{CH_2\text{—}CO}{>}CH$, produced by the successive operations of addition of the two reacting substances, ring closure with the elimination of water, and hydrolysis of the acetyl group in position 4.

Only one of the two possible dibromides is produced by the addition of bromine (1 mol.), and its constitution has not been determined. When its alcoholic solution is heated with 50% aqueous potassium hydroxide on the water-bath, two molecules of hydrogen bromide are eliminated, and a substance, $C_{20}H_{16}O$, pointed prisms, m. p. 181°, is produced, which is regarded as 1-*phenyl*-2 : 5-endo*phenylvinylene*-Δ^1-cyclo*hexen*-3-*one* (annexed formula).



The second substance, $C_{22}H_{24}O_4$, mentioned above, is *β-hydroxy-ζ-keto-β-phenyl-δ-styryloctoic acid*,

$$COMe{\cdot}CH_2{\cdot}CH(CH{:}CHPh){\cdot}CH_2{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2H,$$

produced by the addition of 1 mol. of each of the two reacting substances and of 1 mol. of water. It crystallises in colourless needles, m. p. 120°, forms stable salts (*sodium* salt, $C_{22}H_{23}O_4Na$, needles), and yields a *semicarbazone*, rhombic plates, m. p. 171°, and *phenylhydrazone*, faintly yellow needles, m. p. 134°. Its unsaturated nature is shown by the addition of bromine and by the

instant decolorisation of potassium permanganate by its solution in aqueous sodium carbonate. Under the influence of dilute sodium hydroxide solution, it condenses readily with aromatic aldehydes; the products, however, are not the expected arylidene derivatives produced by condensation at the terminal methyl group, but substances of this composition minus the elements of one molecule of water. The author is of opinion that ring closure, as well as condensation, has occurred, and that the products are *cyclo*hexenecarboxylic acids having the constitution

$$CHPh{:}CH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}C(CH{:}CHAr)\\CH_2\text{——}CPh(OH)\end{matrix}{>}C{\cdot}CO_2H.$$

Benzaldehyde, furfuraldehyde, *p*-tolualdehyde, anisaldehyde, cinnamaldehyde, and *m*-nitrobenzaldehyde all condense in this way and the products are: Ar = Ph, colourless needles, m. p. 193°; $Ar = C_4H_3O$, faintly yellow prisms, m. p. 184°; $Ar = p\text{-}C_7H_7$, colourless prisms, m. p. 194°; $Ar = p\text{-}OMe{\cdot}C_6H_4$, prisms, m. p. 187°; Ar = CHPh:CH, colourless needles, m. p. 191°; and $Ar = m\text{-}NO_2{\cdot}C_6H_4$, yellow needles, m. p. 204°.

Under the conditions given above the reaction between *p*-tolyl cinnamylidenemethyl ketone and acetylacetone is quite similar to that between phenyl cinnamylidenemethyl ketone and acetylacetone. The two products are 1-p-*tolyl*-5-*styryl*-Δ^1-cyclo*hexen*-3-*one*, $C_{21}H_{20}O$, colourless leaflets, m. p. 109° (*semicarbazone*, needles, m. p. 115°), and *β-hydroxy-ζ-keto-β*-p-*tolyl-δ-styryloctoic acid*, $C_{23}H_{26}O_4$, colourless needles, m. p. 106°.

When phenyl cinnamylidenemethyl ketone reacts with benzoylacetone under the conditions given above, only one substance (apart from a considerable quantity of benzoic acid) is produced. This, which is obtained only in small yield, is an acid, $C_{27}H_{26}O_4$, colourless rods, decomp. 185—186°, beginning at about 160°, and is regarded as *β-hydroxy-ζ-keto-βζ-diphenyl-δ-styrylheptoic acid*, $COPh{\cdot}CH_2{\cdot}CH(CH{:}CHPh){\cdot}CH_2{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2H$; it does not condense with aromatic aldehydes in alkaline solution. In the same way *p*-tolyl cinnamylidenemethyl ketone and benzoylacetone react to form only *β-hydroxy-ζ-keto-ζ-phenyl-β*-p-*tolyl-δ-styrylheptoic acid*, $C_{28}H_{28}O_4$, colourless needles, m. p. 167°.

The reaction between phenyl styryl ketone and benzoylacetone under the conditions given above yields Knoevenagel's 1:5-diphenyl-Δ^1-*cyclo*hexen-3-one and an *acid*, $C_{25}H_{22}O_3$, colourless rods, m. p. 202° (decomp. beginning at about 180°), which is regarded as *ζ-keto-βδζ-triphenyl-Δ^α-heptenoic acid*,

$$COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CPh{:}CH{\cdot}CO_2H.$$

Phenyl styryl ketone and acetylacetone react to form 1:5-diphenyl-Δ^1-*cyclo*hexen-3-one and *ζ-keto-βδ-diphenyl-Δ^α-octenoic acid*, which could not be obtained crystalline but forms a *semicarbazone*, $C_{21}H_{23}O_3N_3$, needles, m. p. 170°. C. S.

Preparation of 2-Aminoanthraquinone and its Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 295624; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—2-Aminoanthraquinone and its

derivatives are prepared by heating 2-chloroanthraquinone, or such of its derivatives as do not contain a strongly negative substituent (carboxyl, halogen, nitro-, or sulphonic group) in the ortho-position to the chlorine atom, with aqueous ammonia under pressure, either with or without copper or copper salts. H. W.

Preparation of Benzoyl Derivatives of β-Hydroxy- or αβ-Di- and Poly-hydroxyanthraquinones. R. WEDEKIND & Co. (D.R.-P., 297261; from *J. Soc. Chem. Ind.*, 1917, **36**, 638—639). —The process applies particularly to 2-hydroxyanthraquinone, 2:6- and 1:2-dihydroxyanthraquinone, and 1:2:6- and 1:2:7-trihydroxyanthraquinone, which are treated with benzoic acid with or without the addition of sulphuric acid. The weight of benzoic acid taken is ten to fifteen times that of the hydroxyanthraquinone, and although the sulphuric acid accelerates the reaction, it is not essential. Action is completed by heating the mixture at atmospheric pressure. The process obviates the employment of benzoyl chloride. H. W.

Commercial Chrysarobin. II. ROBERT EDER (*Arch. Pharm.*, 1916, **254**, 1—33. Compare A., 1915, i, 823).—The oxidation products of chrysarobin having been described (*loc. cit.*), the examination of chrysarobin itself has now been undertaken. In order to stabilise its reactive constituents, the chrysarobin (obtained from the same consignment as that used in the oxidation experiments, *loc. cit.*) is first acetylated or benzoylated.

Chrysarobin is boiled for one hour with acetic anhydride and sodium acetate, the solution is poured on ice, and the dark oil is converted by agitation with water into a crude acetate, a brown, friable powder. This is separated by boiling glacial acetic acid into a crystalline orange-yellow powder (*A*), m. p. 230°, and an amorphous substance (*B*), which remains in solution in the acetic acid. The substance *A* agrees in its properties and m. p. with Liebermann's "acetylchrysarobin" (Liebermann's "chrysarobin" and its acetyl derivative [1878—1888] are shown to be, not individual substances, but mixtures of two different anthranols); it, however, contains methoxyl, and is found to be a mixture of triacetylemodinanthranol monomethyl ether (about one-third) and triacetylchrysophanic acid anthranol (about two-thirds). The two constituents cannot be separated by means of solvents, even after hydrolysis, but after demethylation a separation of the products can be effected. The demethylation cannot be brought about by concentrated sulphuric acid, and only imperfectly by a mixture of glacial acetic and concentrated hydrochloric acids at 190°; a boiling mixture of hydriodic acid, D 1·70, and acetic anhydride in equal volumes gives a satisfactory result in the absence of air, and the demethylated product is separated by boiling chloroform into emodinanthranol (yielding emodin by oxidation with chromic acid) and chrysophanic acid anthranol (yielding chrysophanic acid by oxidation).

The composition of the substance *A* has also been ascertained by comparing it with mixtures of triacetylchrysophanic acid anthranol and triacetylemodinanthranol monomethyl ether, separately prepared. These two substances are extraordinarily similar to one another in almost every respect. Their crystals cannot be differentiated under the microscope, they have about the same solubility in the usual solvents, their m. p.'s are almost identical and are lowered by only a few degrees in mixtures of the two substances.

The amorphous substance *B*, which represents about 75% of the product obtained by acetylating chrysarobin, contains a small amount of diacetylemodin monomethyl ether. The main portion, however, is a pale yellow, amorphous powder which, after successive oxidation with chromic and acetic acids at 60° and hydrolysis with boiling 5% alcoholic hydrochloric acid, can be separated by evaporation with a little 10% sodium carbonate solution and extraction of the dried residue with benzene into chrysophanic acid (impure) and emodin.

The m. p. of specially purified diacetylchrysophanic acid is found to be 208°.

An attempt is made to ascertain in what form the chrysophanic acid obtained from the amorphous acetates *B* exists in the original chrysarobin. According to Tutin and Clewer's view, chrysarobin contains, in addition to much chrysophanic acid anthranol, about 5% of chrysophanic acid. The author has been unable to isolate diacetylchrysophanic acid from the amorphous acetates *B*, but by reducing chrysarobin in boiling glacial acetic acid with tin and hydrochloric acid and acetylating the reduced product, he has shown that the amount of triacetylchrysophanic acid anthranol formed is greater than that obtained by acetylating unreduced chrysarobin. This result supports Tutin and Clewer's view, but the author suggests an alternative explanation of the increase.

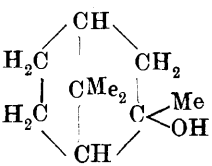
Chrysarobin has been benzoylated in two different ways, which lead to different results. When treated by the Schotten-Baumann method in an atmosphere of hydrogen, chrysarobin yields dibenzoylemodin monomethyl ether (m. p. 233—234°, not 228°, as stated, *loc. cit.*) and dibenzoyldehydroemodinanthranol monomethyl ether, m. p. 235—255° (decomp.), in small quantity, together with considerable amounts of amorphous, unidentified products. In the second method of benzoylation, chrysarobin was boiled with benzoyl chloride until hydrogen chloride ceased to be evolved. After basifying with 20% sodium hydroxide, the product was found to consist mainly of resinous substances, but dibenzoylemodin monomethyl ether and *tribenzoylemodinanthranol monomethyl ether*, $C_{36}H_{23}O_6(OMe)$, yellow prisms, m. p. 265—266°, were isolated. In view of the results obtained by the acetylation of chrysarobin, it is remarkable that tribenzoylchrysophanic acid anthranol is not produced by benzoylation. It has been prepared by heating a pyridine solution of chrysophanic acid anthranol with benzoyl chloride on the water-bath. *Tribenzoylchrysophanic acid anthranol*, $C_{36}H_{24}O_6$, yellow prisms, m. p. 260°, resembles tri-

benzoylemodinanthranol monomethyl ether as closely as the corresponding triacetyl derivatives resemble one another.

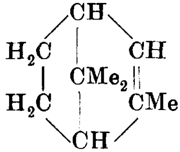
As the results of these experiments and of those previously recorded (*loc. cit.*), the following constituents of chrysarobin have been definitely identified: chrysophanic acid anthranol, emodinanthranol monomethyl ether, emodin monomethyl ether, dehydroemodinanthranol monomethyl ether, and emodin (or emodinanthranol). The author has been unable to detect in his sample of chrysarobin Jowett and Potter's dichrysarobin methyl ether, dichrysarobin, and the substance $C_{17}H_{14}O_4$, Hesse's chrysarobol and chrysophanic acid anthranol methyl ether, and Tutin and Clewer's chrysophanic acid and ararobinol; in other respects his results show an extensive agreement with those of the last-mentioned authors, which were attained by quite different methods. C. S.

Complete Synthesis of a Fenchene. GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennical*, 1916, [*A*], **10**, iii, 3—15; from *Chem. Zentr.*, 1917, i, 751—752).—*α*-Fenchene has been prepared from *α*-fenchocamphorone, thereby completing the synthesis of the former.

α-Fenchocamphorone, b. p. 196—197° (semicarbazone, m. p. 220°), is converted by magnesium methyl iodide into the *alcohol* (annexed formula), b. p. 86·5—87°/14 mm., which, when distilled under atmospheric pressure, loses water and yields *α*-fenchene, b. p. 154—156°, D_4^{20} 0·8660, n_D^{20} 1·47045, M.R. 43·93. The latter is transformed by ozone into *r*-*α*-fenchocamphorone (semicarbazone, m. p. 220°) and a monobasic acid, m. p. 105°, which is identical with *r*-*α*-fenchenylanic acid.



*cyclo*Fenchene hydrochloride, obtained by the action of hydrogen chloride on fenchene, has m. p. 26—29° (Aschan gives m. p. 27·5—29°), and is converted by aniline into *iso*pinene, $C_{10}H_{16}$, b. p. 154—155°, D_4^{20} 0·8671, n_D^{20} 1·47153, M.R. 43·91. It yields a hydrochloride, m. p. 35—37°. When ozonised in acetic acid solution, *iso*pinene yields *α*-fenchocamphorone (semicarbazone, m. p. 219—220) and *r*-*α*-fenchenylanic acid, m. p. 104—105°, identical with the products obtained from *α*-fenchene. The synthetic hydrocarbon and *iso*pinene are therefore identical and constitute *r*-*α*-fenchene (annexed formula). *iso*Pinene is oxidised by alkaline permanganate to *r*-hydroxy-*α*-fenchenic acid, m. p. 139—140°. The fenchenonic acid obtained by Aschan from *iso*pinene (*Öfversigt Finska Vetensk. Soc. Förh.*, 1908—9, [*A*], **51**, No. 9, 10) is probably *apo*camphoric acid contaminated with *dl*-hydroxy-*α*-fenchenic acid.



Wallach's *r*-*α*-fenchene (A., 1908, i, 811) on ozonisation yields *α*-fenchocamphorone and *r*-*α*-fenchenylanic acid, m. p. 105°.

Sodium hypobromite solution transforms *r*-hydroxy-*α*-fenchenic acid, m. p. 140°, into fenchocamphorone, which is further con-

verted into a product, m. p. 50—54° (probably a bromofenchocamphorone), and an *acid*, m. p. 147—148°, which contains bromine. *apo*Camphoric acid could not be identified. The observation of Aschan (*loc. cit.*) that bromoform is eliminated during this action is probably erroneous, since the odour of fenchocamphorone and hypobromite solution resembles that of bromoform.

r-α-Fenchene hydrochloride, obtained from Wallach's α-fenchene and hydrogen chloride, has m. p. 35—37°, b. p. 81°/12 mm., and then m. p. 33—35°; it does not depress the m. p. of the hydrochloride prepared from *iso*pinene. H. W.

The Oleoresin of Douglas Fir. A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1040—1044. Compare Rabak, *Pharm. Rev.*, 1904, **22**, 293).—Samples of oleoresin were obtained from the heartwood and living wood of the Douglas fir. The oleoresin from the heartwood contained a volatile oil consisting chiefly of highly rotatory *l*-α-pinene with small amounts of *l*-limonene and *l*-terpineol. That from the sapwood contained an oil consisting of *l*-α-pinene, *l*-β-pinene, and probably a little *l*-limonene. The so-called firpene described by Frankforter and Frary (compare A., 1906, i, 970, 971) as occurring in this oleoresin is probably highly active *l*-α-pinene, the activity accounting for the fact that no nitrosochloride was obtained from it (compare Tilden, T., 1904, **85**, 759). W. G.

Further Syntheses of Glucosides by Means of Acetobromoglucose and Quinoline. Derivatives of Menthol and Resorcinol. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1917, **50**, 711—722. Compare this vol., i, 216).—The α- and β-glucosides of menthol and their acetates, and the penta-acetate of the β-glucoside of resorcinol, have been prepared, starting with acetobromoglucose, quinoline, and menthol or resorcinol. α-Menthylglucoside can be obtained more easily than any other synthetic glucoside of a cyclic compound known as yet, and will undoubtedly be of interest for physiological studies.

Acetobromoglucose (50 grams), *l*-menthol (110), and quinoline (20) are heated at 100—105°, the base is extracted with dilute sulphuric acid and ether, the washed ethereal solution is evaporated, and the water and excess of menthol removed by heating at 100°/0·2 mm. The product is a mixture of the tetra-acetates and lower acetates of the α- and β-glucosides. For the purpose of isolating the tetra-acetates, the mixture is acetylated by means of acetic anhydride and pyridine in the cold, and then the glucosides are separated by crystallisation from dilute alcohol. Tetra-acetyl-β-menthylglucoside separates first, in long, flat, glistening needles, m. p. 131—132° (corr.), $[\alpha]_D^{17}$ $-66·0°$ in benzene, and β-menthylglucoside can be readily obtained from this by means of aqueous-alcoholic barium hydroxide at 60°, in large plates, $1H_2O$, m. p. 75—76°, which lose water at 56°/15 mm., and then have $[\alpha]_D^{20}$ $-93·7°$, in alcohol (compare A., 1909, i, 365). The more

soluble *tetra-acetyl-α-menthylglucoside* crystallises in stellate aggregates of prisms, m. p. 82—83°, $[\alpha]_D^{20}$ +94·4°, in benzene.

Triacetates can be isolated by fractional crystallisation from the original crude product. *Triacetyl-β-menthylglucoside* separates in radiating needles, m. p. 143° (corr.), $[\alpha]_D^{18}$ −12·73°, and *triacetyl-α-menthylglucoside* in large, flat prisms, m. p. 99—100°, $[\alpha]_D^{20}$ +107·5°.

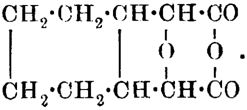
α-Menthylglucoside, $C_{16}H_{30}O_6,H_2O$, is very sparingly soluble in cold water, and crystallises quickly from 2000 parts of hot water on cooling. For this reason it is very easily isolated, and so the crude mixture obtained at the outset, or the triacetates, or the still lower acetates left in the mother liquors may be worked up for this glucoside. Starting with acetobromoglucose, the yield of α-menthylglucoside may be as much as 50%. It crystallises from acetone in prisms, m. p. 159—160° (corr.), $[\alpha]_D^{20}$ +64·2° in alcohol.

The hydrolysis of α- and β-menthylglucosides was tested in the usual way. The β-glucoside is somewhat more rapidly hydrolysed by acids than the isomeride, and yeast extract and emulsin also behave normally.

With resorcinol, the mixture of acetyl derivatives obtained by the above method is so complex that it is best to acetylate it completely to *penta-acetyl-β-resorcinolglucoside* (*tetra-acetyl-β*-m-*acetoxyphenylglucoside*) by means of acetic anhydride and pyridine. This crystallises in long, radiating needles or prisms, m. p. 118—119° (corr.), $[\alpha]_D^{18}$ −40·1°, in benzene. The known β-resorcinolglucoside (A., 1912, i, 884) is then conveniently obtained by hydrolysis with barium hydroxide. J. C. W.

Digitalis Glucosides. H. Kiliani (*Arch. Pharm.*, 1916, **254**, 255—295).—An account of work already published (A., 1915, i, 281; 1916, i, 493; also A., 1914, i, 309, 857). C. S.

Cantharidin. V. Walter Rudolph (*Arch. Pharm.*, 1916, **254**, 423—456).—In some cases one, in other cases another, of the three formulæ for cantharidin proposed by Gadamer (*Arch. Pharm.*, 1914, **252**, 609) serves to explain the reactions described by the author in this and in his preceding paper (*ibid.*, 636). Before a preference in favour of any one of the three formulæ can be expressed, the constitutions of cantharene and of the acid obtained by the pyrogenic decomposition of barium cantharate must be determined. The author attacks the former problem, leaving the latter to Gadamer. He also examines the substance $C_{10}H_{14}O_3$, which he calls *cantharidide*, obtained by Anderlini in 1893 by reducing cantharidin by sodium and ethyl alcohol. This proves to be a neutral substance exhibiting the properties of a very stable lactone, and is not identical with the product obtained by the reduction of the "dibromide" of cantharidin. In the author's opinion, these facts serve to eliminate the second of Gadamer's three formulæ (annexed).



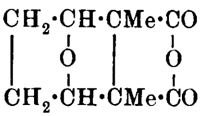
The acid anhydride group of cantharidin is so stable that the corresponding acid, cantharidic acid, cannot be isolated and is

only known in aqueous solution. When the "dibromide" is reduced by zinc and zinc dust in acetic and dilute sulphuric acids, the product possesses this property to a very much less pronounced degree, and the acid itself, *deoxycantharidic acid*, $C_{10}H_{16}O_4$, crystals, m. p. 160—165° to a turbid liquid, can be isolated, although it is still contaminated with 10—15% of the anhydride, *deoxycantharidin*. The acid, which forms a *silver* salt,

$$C_{10}H_{14}O_4Ag_2,H_2O,$$

cannot be converted, curiously enough, into its anhydride by heating in a vacuum at 70°; the change is effected, however, by fusion or by boiling with water. Deoxycantharidin is a colourless, friable substance which is slowly volatile with steam and has an odour recalling that of camphor. Attempts to resolve deoxycantharidic acid into optically active components by means of the brucine salt were unsuccessful.

The "dibromide" of cantharidin is converted by methyl-alcoholic hydrogen bromide, even after keeping for a week, only into a *methyl hydrogen* ester, $C_{11}H_{16}O_4Br_2$, m. p. 122°, becoming turbid at 120°; when the preparation is conducted with methyl-alcoholic hydrogen chloride on the water-bath, a liquid *substance* ($C_{11}H_{15}O_4Br$?), b. p. 132—133°/14 mm., is obtained, which appears to be the methyl hydrogen ester deprived of the elements of 1 molecule of hydrogen bromide. The failure of the "dibromide" of cantharidin to yield a dimethyl ester is attributed to steric hindrance, and on this account the preference is given to the formula (annexed) of Gadamer's remaining two formulæ of cantharidin. This preference is supported by the fact that cantharene, prepared by boiling the "dibromide" of cantharidin with 25% aqueous potassium hydroxide in an atmosphere of hydrogen, has a smaller exaltation of the molecular refraction than the values previously recorded (compare Haworth, T., 1913, **103**, 1242). The author has not succeeded in obtaining *o*-toluic acid by the oxidation of cantharene under Piccard's conditions. C. S.



Formation of Hydrocoumarin Derivatives (Dihydro-α-benzopyrones) from Phloroglucinol. EMIL FISCHER and OSMAN NOURI (*Ber.*, 1917, **50**, 693—701).—Whereas ordinary nitriles give rise to ketones when condensed with phloroglucinol by Hoesch's method (A., 1915, i, 820; this vol., i, 342), unsaturated nitriles yield derivatives of dihydrocoumarin. Unstable imines are formed as intermediate products, as in the production of γ-benzopyrones by the condensation of acylacetonitriles with pyrogallol (Ghosh, A., 1916, i, 281), but these are readily hydrolysed by water to the α-benzopyrone derivatives.

Cinnamonitrile and phloroglucinol are dissolved in ether, mixed with powdered zinc chloride, and the chilled solution saturated with hydrogen chloride. The granular hydrochloride of the intermediate imine (I.) gradually separates and this yields 5 : 7-*dihydroxy*-4-*phenyl*-3 : 4-*dihydro*-1 : 2-*benzopyrone* (II.) on heating with

water. The compound crystallises in slender needles, m. p. 211° (corr.) and forms a *diacetate*, m. p. 147—148° (corr.).

$$C_6H_3(OH)_3 + CHPh{:}CH{\cdot}CN + HCl \longrightarrow$$

$$C_6H_2(OH)_2{<}\begin{matrix}CHPh{\cdot}CH_2 \\ O\text{———}C{:}NH,HCl\end{matrix} \longrightarrow C_6H_2(OH)_2{<}\begin{matrix}CHPh{\cdot}CH_2 \\ O\text{———}CO\end{matrix}.$$

(I.) (II.)

The same substance can be obtained by the reduction of the corresponding 5 : 7-dihydroxy-4-phenyl-1 : 2-benzopyrone ("*m*-dihydroxy-β-phenylcoumarin"; Kostanecki and Weber, A., 1894, i, 88). When treated with diazomethane, it gives rise to the 5 : 7-*dimethoxy*-derivative, which crystallises in long needles or stout prisms, m. p. 131—132° (corr.). This may be converted into *β-phenyl-β-2 : 4 : 6-trimethoxyphenylpropionic acid*, large columns or tablets, m. p. 156—157° (corr.), by first opening the ring by hydrolysis with aqueous-alcoholic sodium hydroxide, methylating the free acid obtained, by adding the ethereal extract to cold ethereal diazomethane, and finally hydrolysing the methyl ester. The 5 : 7-dimethoxy-compound may also be transformed into *β-phenyl-β-2-hydroxy-4 : 6-dimethoxyphenylpropionamide*, m. p. 185—186° (decomp.), by the action of methyl-alcoholic ammonia at 50—60° in a sealed tube, or into *β-phenyl-β-2-hydroxy-4 : 6-dimethoxyphenylpropion-ω-phenylhydrazide*,

$$OH{\cdot}C_6H_2(OMe)_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NHPh,$$

long prisms, m. p. 171—172° (corr.), by warming with phenylhydrazine.

p-Coumaronitrile condenses with phloroglucinol under the above conditions to form 5 : 7-*dihydroxy*-4-p-*hydroxyphenyl*-3 : 4-*dihydro*-1 : 2-*benzopyrone*, which crystallises in slender needles, m. p. indefinite, about 270°.

Ethyl phenylpropiolate condenses with phloroglucinol to give a high yield of the above-mentioned 5 : 7-dihydroxy-4-phenyl-1 : 2-benzopyrone, m. p. 238—239° (corr.). J. C. W.

Alkaloidal Derivatives of Mercuric Nitrite. PRAFULLA CHANDRA RÂY (T., 1917, **111**, 507—510. Compare T., 1912, **101**, 616).—Compounds of mercuric nitrite with aliphatic and aromatic amines and with heterocyclic bases have already been obtained (*loc. cit.*), and the author now describes compounds with various alkaloids, viz., nicotine, coniine, quinine, quinidine, cinchonidine, codeine, narcotine, strychnine, brucine, and cocaine. Experiments on the electrical conductivity of aqueous solutions of the cinchonidine and cocaine compounds, which contain the alkaloid and mercuric nitrite in molecular proportion, indicate the formation of three ions in each case.

For experimental details see the original. D. F. T.

Aconite Alkaloids. Pyraconitine and Pyraconine. HEINRICH SCHULZE and A. LIEBNER (*Arch. Pharm.*, 1916, **254**, 567—583).—Pyraconitine, obtained by heating aconitine or japaconitine at 192°

(A., 1913, i, 1375), does not interact with ketone reagents, but forms a *diacetyl* derivative,

$$C_{20}H_{21\,(or\,19)}O(NMe)(OMe)_4(OAc)_2{\cdot}OBz,$$

stout crystals containing 1EtOH from alcohol, m. p. 213°, softening at about 202° (dried, m. p. 208°), which forms an *aurichloride*, yellow crystals, decomp. 214°; *hydriodide*, stout needles, m. p. 260·5°; and *perchlorate*, crystals, m. p. 282—283° (decomp.).

The remaining uncharacterised oxygen atom in pyraconitine is present probably in the ethylene oxide form, since it is unaffected by ketone reagents, by acylating reagents, and by water at 192°; by heating pyraconitine with methyl alcohol at 130° methyl benzoate and pyraconine are formed, whilst methyl iodide at 100° has no action.

Since Dunstan and Carr's pyraconitine (T., 1894, **65**, 176) is identical with Dunstan and Read's pyrojapaconitine (T., 1900, **77**, 60), it follows that the pyraconine prepared from the former must be identical with the pyrojapaconine prepared from the latter. This is shown to be the case. Pyraconine has not been obtained crystalline, but it forms well-crystallised salts; the hydrochloride forms large crystals containing $2\frac{1}{2}H_2O$, m. p. 134—135° (decomp.), $[\alpha]_D$ −124·6° in aqueous solution (Dunstan and Carr give m. p. 154° and $[\alpha]_D$ −102·07°); the *hydrobromide* forms stout crystals containing $2H_2O$, decomp. 143° (anhydrous, 146—147°); the *hydriodide* forms crystals containing $1H_2O$, m. p. 224·5° (decomp.); and the *perchlorate* forms anhydrous crystals, darkening at 235°, m. p. 243°, decomp. 244°.

Four of the oxygen atoms in pyraconine are present in methoxy groups. Three of the remaining four are present in hydroxyl groups, since *triacetylpyraconine*, $C_{31}H_{45\,(or\,43)}O_{11}N$, stout colourless prisms, m. p. 231°, has been prepared.

Pyraconitine does not undergo reduction when it is treated by the Paal-Skita method. Its hydrobromide appears to exist in two different forms, which are only distinguishable by their m. p.'s, 150° (decomp.) (anhydrous, 177°) and 240° (decomp. at 242°) (anhydrous, 243—244° [decomp.]) respectively, the m. p. of the mixture being about 150°. C. S.

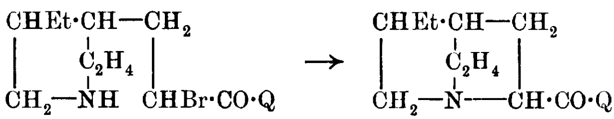
The Cinchona Alkaloids. ADOLF KAUFMANN (*Ber.*, 1917, **50**, 701—702).—A claim for priority over Rabe (compare this vol., i, 216). J. C. W.

The Influence of Varying Concentration of Hydrogen Ion on the Optical Rotation of the Isomeric Alkaloids, Cinchonine, Cinchonidine and Cinchotoxine. H. C. BIDDLE and THOMAS WATSON (*J. Amer. Chem. Soc.*, 1917, **39**, 968—974. Compare A., 1915, ii, 759).—The specific rotation in the case of these three alkaloids is a direct function of the concentration of the bivalent alkaloid ion and is independent of the inactive acid ion. The univalent cinchonine ion has $[\alpha]_D^{16} = +205·6°$ and the bivalent ion $[\alpha]_D^{16} = +253·1°$. The corresponding values for the cinchonidine ions are $[\alpha]_D^{16} = -141·1°$ and −185·6° respectively. The value of

the second dissociation constant of cinchonine at 16° was found to be $2{\cdot}05 \times 10^{-10}$ (compare Veley, T., 1908, **93**, 2114; 1909, **95**, 758).

W. G.

Quinaketones. ADOLF KAUFMANN and PAUL HAENSLER (*Ber.*, 1917, **50**, 702—705. Compare A., 1913, i, 1222).—When cinchoticine (originally "dihydrocinchotoxine") is treated with bromine in hydrobromic acid solution, it yields bromocinchoticine dihydrobromide, from which a *monohydrobromide*, m. p. 194—195°, has now been obtained by the application of the calculated quantity of sodium hydrogen carbonate. The free brominated base (I.) cannot be isolated, however, for the tendency to the closure of the quinuclidine ring is too strong. The product, cinchotinone ("hydrocinchoninone") II., forms a *hydriodide*, m. p. 196°, and the *hydriodide* of an iso-*methiodide*, yellowish-red leaflets or needles, m. p. 214—215°.



(I.) (II.)

[Q = Quinolyl.]

Cinchotinone may also be brominated in chloroform solution, the halogen replacing the hydrogen atom adjacent to the carbonyl group. *Bromocinchotinone* crystallises in yellow needles, m. p. 161—162°.

J. C. W.

Corydalis Alkaloids. XIV. *r*-Corydaline. J. GADAMER [and, in part, WALTER KLEE] (*Arch. Pharm.*, 1916, **254**, 295—305). —Gadamer and Wagner have shown (A., 1902, i, 307) that the reduction of dehydrocorydaline leads to the formation at times of an optically inactive corydaline, m. p. 158—159°, in addition to Ziegenbein's optically inactive corydaline, m. p. 135°. Later Gadamer and Haars produced evidence indicating that the latter is to be regarded as *r*-corydaline and the former as *r*-mesocorydaline (A., 1905, i, 462), the two compounds being stereoisomeric. The conditions have now been established under which either substance can be obtained at will. *r*-Corydaline alone is produced, but not quantitatively, when an aqueous solution of dehydrocorydaline hydrochloride is reduced by platinised zinc and dilute sulphuric acid on the water-bath; amongst the other products of the reaction is found a phenolic base, m. p. 220—224°, which exhibits the properties and colour reactions of *i*-corybulbine. Under milder conditions of reduction, by keeping an alcoholic solution of dehydrocorydaline hydrochloride with zinc dust and sulphuric acid for several days at the ordinary temperature until it is decolorised, a very good yield of nearly equal quantities of *r*-mesocorydaline and *r*-corydaline is obtained; the separation of the two bases is easily effected since *r*-mesocorydaline alone crystallises from an ethereal solution of the mixture.

r-Mesocorydaline forms a hydrochloride containing $1H_2O$

(Gadamer and Haars state $2H_2O$, *loc. cit.*), m. p. 238—240° (decomp.) or 247—248° (anhydrous); *sulphate*, small crystals; *nitrate*, well-formed, anhydrous crystals, decomp. 207—208°; *aurichloride*, reddish-yellow needles, m. p. 191—192° (decomp.); and *platinichloride*, amorphous.

Although *r*-mesocorydaline has been resolved into active components (the *d*-form is not identical with natural *d*-corydaline), attempts to resolve *r*-corydaline have failed (Gadamer, A., 1911, i, 153). It can be sulphonated in the same way as natural *d*-corydaline (Gadamer and Wagner, *loc. cit.*) and yields r-*corydalinesulphonic acid*, glistening leaflets, m. p. above 300°. This is easily resolved by means of brucine, calculated quantities of the acid and the base in warm dilute alcohol yielding on cooling *brucine* l-*corydalinesulphonate*, stout leaflets containing $4H_2O$. l-*Corydalinesulphonic acid* also crystallises in leaflets and when neutralised by *N*/10-potassium hydroxide has $[\alpha]_D$ −153·5°. Since the *d*-sulphonic acid obtained from natural corydaline has $[\alpha]_D$ +150·3° under the same conditions, the inactive corydaline, m. p. 135°, is indubitably proved to be *r*-corydaline.

r-*Mesocorydalinesulphonic acid*, rosettes of slender needles, is obtained in the same way as *d*-corydalinesulphonic acid (*loc. cit.*). It cannot be resolved by means of the brucine salt.

When *d*-corydalinesulphonic acid is boiled with an alcoholic solution of iodine the consumption of iodine corresponds with the removal of only two atoms of hydrogen (not of four, as the authors had anticipated) and *didehydrocorydalinesulphonic acid*,

$$C_{22}H_{25}O_7NS,$$

colourless crystals with $5H_2O$, is obtained. This develops a magnificent bluish-green fluorescence in concentrated sulphuric acid and is strongly lævorotatory in solution. The significance of this change of sign in the rotation is discussed and the formula

$$SO_3H\cdot C_6H(OMe)_2<\begin{matrix}CH{=\!=}C\cdot C_6H_2(OMe)_2\\ \quad\quad\;\; | \\ CHMe\cdot N\cdot CH_2\text{———}\end{matrix}>CH_2$$

is ascribed to the substance for reasons stated in the paper.

C. S.

Methyl Derivatives of Morphine. C. MANNICH (*Arch. Pharm.*, 1916, **254**, 349—363).—According to the constitution of morphine proposed by Knorr and Pschorr, the alkaloid functions as a tertiary base, as a phenol, and as a secondary alcohol. Theoretically, therefore, one trimethyl, three dimethyl, and three monomethyl derivatives should be capable of existence. Four of these are already known and the remaining three are now described.

Although Pschorr and Dickhäuser's methylcodeine methiodide (A., 1911, i, 908) undergoes extensive decomposition by heating, the corresponding *methochloride*, $C_{20}H_{26}O_3NCl$, colourless crystals, m. p. 208° (*picrate*, yellow needles, m. p. 211—212°; *platinichloride*, yellow needles, decomp. about 215°), loses methyl chloride by heating under 2 mm. pressure and yields *morphine OO-dimethyl ether*, $C_{17}H_{17}ON(OMe)_2$, prismatic or tabular crystals, m. p. 140—141°. This method of demethylating quaternary bases is unfortunately

not applicable to any other morphine derivative. A second method of preparing the same dimethyl ether is the following. Morphine oxide or codeine oxide is shaken with a large excess of *N*-sodium hydroxide and methyl sulphate at 0°, the solution is faintly acidified with hydrochloric acid and treated with concentrated aqueous potassium iodide, and the crystalline substance obtained, m. p. about 253° (doubtless the hydriodide of morphine oxide dimethyl ether), is heated at about 80° with sulphurous acid and a little sodium hydrogen sulphite, and the solution is basified and extracted with ether, whereby morphine OO-dimethyl ether, identical with that mentioned above, is obtained. It has not been converted into thebaine by oxidation, but yields methylcodeine methiodide by treatment with chloroform and methyl iodide, and its hydrochloride in aqueous solution is reduced by hydrogen and palladinised charcoal to *dihydromorphine dimethyl ether hydrochloride*, $C_{17}H_{19}ON(OMe)_2,HCl,3H_2O$, small plates, m. p. about 116°.

Morphine methoxymethyl ether, $C_{17}H_{17}ON(OH)(O{\cdot}CH_2{\cdot}OMe)$, colourless needles, m. p. 94—96°, obtained by treating a suspension of the sodium derivative of morphine in cold chloroform with chloromethyl ether, is insoluble in alkali hydroxides, does not give a coloration with ferric chloride, but instantly develops a violet coloration (the morphine–formaldehyde reaction) with concentrated sulphuric acid. It is stable towards alkalis, but is converted by dilute acids into morphine, formaldehyde, and methyl alcohol. The *sulphate*, $2C_{19}H_{23}O_4N,H_2SO_4$, forms crystals containing $10H_2O$, and the *methiodide* tufts of needles, m. p. 225° (decomp.). When the ether is shaken with an excess of *N*-sodium hydroxide and methyl sulphate at 0° and the product is treated with cold, concentrated aqueous potassium iodide, *morphine* O-*methoxymethyl* O-*methyl ether methiodide*, $OMe{\cdot}CH_2{\cdot}O{\cdot}C_{17}H_{17}O(OMe)N,MeI$, crystals, decomp. about 253°, is obtained. The corresponding *methochloride*, $C_{21}H_{28}O_4NCl$, decomp. about 200°, is converted by warming with sulphurous acid and a little sodium hydrogen sulphite into *heterocodeine methochloride*,

$$OH{\cdot}C_{17}H_{17}O(OMe)NMeCl,$$

colourless crystals, m. p. above 270°, which does not give a violet coloration with concentrated sulphuric acid but develops a blue coloration with aqueous ferric chloride. The methochloride cannot be converted into *heterocodeine* (this is the name given by the author to the monomethyl ether of morphine methylated at the secondary alcoholic group), which is obtained, however, by the following method. Morphine methoxymethyl ether is gently warmed with hydrogen peroxide, and the resulting syrup, which doubtless contains an amino-oxide, is treated with *N*-sodium hydroxide and methyl sulphate at 0°, and the resulting solution is acidified with dilute sulphuric acid and treated with concentrated aqueous potassium iodide solution; the precipitate is collected and warmed with sulphurous acid for two days, whereby *heterocodeine*, $OH{\cdot}C_{17}H_{17}ON(OMe)$, crystals, m. p. 242°, is obtained, which is isolated as the *hydrochloride*, prisms containing $2H_2O$, m. p. 102°.

Heterocodeine is soluble in alkali hydroxides, develops a blue coloration with ferric chloride and a reddish-violet coloration with formaldehyde and sulphuric acid, and is shown to be a true derivative of morphine, not of *iso*- or *ψ*-codeine, by its conversion by diazomethane into morphine OO-dimethyl ether. C. S.

Preparation of Cephaeline Amyl Ethers and Salts thereof. J. W. MEADER (Brit. Pat., 105722, 1916; addition to Brit Pat., 103881; from *J. Soc. Chem. Ind.*, 1917, **36**, 615. Compare this vol., i, 348).—*Cephaeline amyl ethers* other than the *iso*amyl ethers, which form the subject of the principal patent, are produced by treating cephaeline with an alkali metal and an amyl haloid. The process is the same as that described in the principal patent, and the product has similar properties. H. W.

Preparation of 3-Nitrocarbazole and its Halogen Derivatives. AKTIEN GESELLSCHAFT FUR ANILINFABRIKATION (D.R.-P., 295817; from *J. Soc. Chem. Ind.*, 1917, **36**, 542).—3-Nitrocarbazole and its halogen derivatives are obtained by treating carbazole or its halogen substitution products with about two molecules of nitric acid (10%). H. W.

Preparation of Arylalkylhydantoins. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat., 105719; from *J. Soc. Chem. Ind.*, 1917, **36**, 615).—Arylalkylhydantoins of the general formula $\begin{matrix}Ar\\Alk\end{matrix}\!>C<\!\begin{matrix}NH\cdot CO\\ \vert \quad\ \ \vert\\ CO-NH\end{matrix}$ are produced in the same manner as other hydantoins or cyclic ureides, starting from arylalkylaminoacetic acids, or causing the latter to be produced during the process. They are therapeutically valuable on account of their hypnotic action. Eight methods of preparation are described. Thus, ethyl α-amino-α-phenylbutyrate (20 parts) is neutralised with dilute hydrochloric acid and a concentrated solution of potassium cyanate (8 parts) is added. After a short time the solution is boiled, when *phenylethylhydantoin*, m. p. 198°, separates. It forms soluble alkali and alkaline-earth salts. Alternatively, cyanophenylacetamide is transformed into *phenylethylcyanoacetamide*, m. p. 120°, by the action of ethyl bromide in the presence of alcoholic sodium ethoxide; the latter is added to a solution of sodium hypobromite, heated to 40°, and cooled; after treatment with sodium hydrogen sulphite solution, phenylethylhydantoin is precipitated by acidifying with hydrochloric acid. *Phenylmethylhydantoin*, *piperonylmethylhydantoin*, and p-*chlorophenylethylhydantoin* have m. p. 193°, 192—193°, and 212° respectively. H. W.

Hydantoins. XXXIX. Synthesis of the Polypeptide-hydantoin; Tyrosylglycine-hydantoin. TREAT B. JOHNSON and DOROTHY A. HAHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1255—1266. Compare Johnson and Bates, A., 1916, i, 504).—It has already

been suggested that the fibroin molecule may contain "polypeptide-hydantoins," and as fibroin on hydrolysis yields a large proportion of glycine and tyrosine, the preparation of tyrosylglycine-hydantoin was undertaken.

4-Anisylidenehydantoin (Wheeler and Hoffmann, A., 1911, i, 499) and its reduction product, 4-anisylhydantoin (Johnson and Nicolet, A., 1912, i, 585), when treated with ethyl chloroacetate in alkaline solution are converted into *ethyl* 4-*anisylidenehydantoin*-1-*acetate*, $\begin{matrix} CO_2Et\cdot CH_2\cdot N - CO \\ CO\cdot NH \end{matrix}\!\!>C\!:\!CH\cdot C_6H_4\cdot OMe$, needles, m. p. 178°, and *ethyl* 4-*anisylhydantoin*-1-*acetate*, needles, m. p. 138°, respectively; the latter product is also obtainable by reduction of the former in alcoholic solution with tin and hydrochloric acid, and both esters are hydrolysable to the corresponding *acids*, plates, m. p. 271°, and prisms, m. p. 166° (*potassium* salt, plates, decomp. near 260°), respectively. The anisylidenehydantoinacetic acid appeared to be capable of existence in an *isomeric* form, the aqueous solution under certain conditions depositing a substance of similar external appearance, but of no m. p. below 315°. When treated in hot alcoholic solution with a bimolecular proportion of potassium hydroxide, ethyl 4-anisylhydantoin-1-acetate was converted into s-*glycine*-p-*methoxyphenylalaninocarbamide*,

$$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OMe,$$

plates, m. p. 161° (decomp.) (*dipotassium* salt), which readily yields 4-anisylhydantoin-1-acetic acid on heating with hydrochloric acid.

The polypeptide-hydantoin, namely, 4-*hydroxybenzylhydantoin*-1-*acetic acid*, $\begin{matrix} CO_2H\cdot CH_2\cdot N - CO \\ CO\cdot NH \end{matrix}\!\!>CH\cdot CH_2\cdot C_6H_4\cdot OH$, rosettes of compact crystals, m. p. 217—218° (*ethyl* ester, needles, m. p. 195°), was obtainable from 4-anisylidenehydantoin-1-acetic acid or its ester by reduction with hydriodic acid or with tin and hydrochloric acid, and also from 4-anisylhydantoin-1-acetic acid and its ester by heating with hydrobromic acid; the latter process gave rise to the *ethyl* ester, needles, m. p. 195°, as an intermediate product, the methoxy-group undergoing scission before the ester group. When hydrolysed with hydrochloric acid, 4-hydroxybenzylhydantoin-1-acetic acid or its ester gave rise to ammonia, carbon dioxide, and tyrosine, whilst treatment with alcoholic potassium hydroxide yielded the *dipotassium* salt (compact crystals) of unstable s-*tyrosineglycinecarbamide*,

$$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH,$$

which readily underwent reconversion into the polypeptide-hydantoin. D. F. T.

Synthesis of *r*-2-Methyltryptophan. GEORGE BARGER and ARTHUR JAMES EWINS (*Biochem. J.*, 1917, **11**, 58—63).—The first step in the synthesis of this methyltryptophan is the preparation of 2-methylindole-3-aldehyde from 2-methylindole, which is accomplished by Gattermann's hydrocyanic acid method with a 75% yield (compare Plancher and Ponti, A., 1907, i, 341). From this

aldehyde the synthesis closely follows that of tryptophan by Ellinger and Flamand (A., 1907, i, 737). The *azlactone* of *α-benzoylamino-β-2-methylindolylacrylic acid*,

$$\begin{array}{l} C_6H_4{\cdot}C{\cdot}CH{:}C{\cdot}N{:}CPh \\ NH{-}CMe\quad CO{-}O \end{array},$$

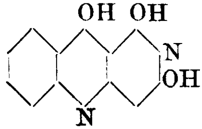
is formed by the interaction of the aldehyde and hippuric acid in the presence of anhydrous sodium acetate and acetic anhydride, and on recrystallisation from glacial acetic acid or chloroform gives orange-yellow prisms which sinter at 202° and melt at 211°. The corresponding acid, *α-benzoylamino-β-2-methylindolylacrylic acid*, $C_{19}H_{16}O_3N_2$, crystallises from 70% alcohol in pale yellow, prismatic needles, m. p. 221—222°. The acid is reduced by dissolving in alcohol and treating with sodium, and the benzoyl group then removed by boiling after the addition of a little water. The resulting r-2-*methyltryptophan*, $\begin{array}{l} C_6H_4{\cdot}C{-}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \\ NH{-}CMe \end{array}$ crystallises with 1MeOH from methyl alcohol and ether in colourless prisms, m. p. 263—273°, according to the rate of heating. It gives a strong reaction with triketohydrindene hydrate. With excess of bromine water a precipitate is produced, but not a coloration, which indicates that the bromine reaction of natural tryptophan probably consists of an attack on the α-carbon atom of the indole ring. The reactions with Hopkins and Cole's reagent and with glyoxylic acid are given only by relatively strong solutions of methyltryptophan. Methyltryptophan has a sweet taste and yields a picrate, $C_{12}H_{14}O_2N_2,C_6H_3O_7N_3$, orange-red plates, from methyl alcohol and light petroleum, m. p. 173°.

In a feeding experiment, the urine of a dog after the administration of 0·5 gram of methyltryptophan contained an indole derivative, but neither kynurenic acid nor a similar substance. The authors are therefore unable to draw definite conclusions as to the mechanism of the production of kynurenic acid from tryptophan (compare Asayama, A., 1916, i, 860). H. W. B.

Synthesis of 1 : 3 : 10-Trihydroxybenzo-2 : 5-naphthyridine [1 : 3 : 10-Trihydroxy-2 : 5-naphthadiazine] and its Conversion into Kynurenic Acid. St. von Niementowski and Ed. Sucharda (*J. pr. Chem.*, 1916, [ii], **94**, 193—227).—Details are given of the best conditions for preparing glutazine from ethyl β-amino-β-hydroxy-γ-carbamylbutyrate by the method of von Pechmann and Stokes (1885). The mother liquors are found to contain the *sodium* salt, $C_5H_4O_3NNa,2H_2O$, of 2 : 4 : 6-trihydroxypyridine, orange, sandy, crystalline powder, so that the yield of this substance, from this source and from the hydrolysis of the glutazine, amounts to 55% of that theoretically obtainable. The trihydroxypyridine forms a *diacetyl* derivative, faintly yellow needles, m. p. 247°.

When a mixture of anthranilic acid (2 mols.) and glutazine or 2 : 4 : 6-trihydroxypyridine (1 mol.) is heated from 130° to 160° during three hours, only one product is obtained. The condensa-

tion follows the same course in acetic acid or neutral aqueous solution at the b. p., but fails in alkaline or in mineral acid solution. The formation of only one product is quite unexpected, since phloroglucinol yields at least three products by condensation with anthranilic acid. The product, $C_{12}H_8O_3N_2$, yellow, metallic needles, m. p. 370°, is regarded as 1:3:10-*trihydroxybenzo*-2:5-*naphthyridine* (annexed formula), since it yields 4-hydroxy-2-methylquinoline quantitatively by heating with hydrochloric acid, D 1·1, at 245°. The substance, which is the first representative of this class of compound, has pronounced acid properties (*potassium* salt, $C_{12}H_7O_3N_2K,3\frac{1}{2}H_2O$, yellow needles, becoming dirty violet at 110°), but its salts with mineral acids are unstable and easily hydrolysed (*hydrochloride*, $C_{12}H_8O_3N_2,HCl,2H_2O$, golden-yellow needles). It forms an *acetyl* derivative, $C_{12}H_7O_3N_2Ac$, yellow, microcrystalline plates, m. p. about 373°, *dibenzoyl* derivative, cream-coloured, microcrystalline plates containing $1C_5H_5N$ (the substance is prepared in the presence of pyridine), and p-*nitrobenzeneazo*-derivative, $C_{18}H_{11}O_5N_5$, yellowish-bronze, microcrystalline powder, becoming brick-red when powdered, m. p. 336°. The dibenzoyl derivative loses its pyridine at 117—122° and becomes flesh-coloured, and then cream-coloured again; when heated in a capillary tube, it softens at 160° and has m. p. about 205°. By crystallisation from a cold benzene solution, the dibenzoyl derivative separates in yellowish-white, microcrystalline needles, which do not contain pyridine, have m. p. 235°, and are changed into the preceding, pyridine-containing form by solution in pyridine and precipitation with water. These phenomena are probably to be explained by the change from the trihydroxy- to the triketo-structure.



The trihydroxybenzonaphthyridine forms a *sulphonic acid*, $C_{12}H_7O_3N_2(SO_3H)$, aggregates of golden- or brownish-yellow prisms containing $4H_2O$, which carbonises at 350—390°.

According to the experimental conditions, three different products are obtained by the oxidation of 1:3:10-trihydroxybenzo-2:5-naphthyridine by potassium permanganate. By triturating a mixture of the two solids for ten minutes, the chief product is 4-*hydroxyquinoline*-2 : 3-*dicarboxylimide*, $OH\cdot C_9H_4N{<}^{CO}_{CO}{>}NH$, golden-yellow leaflets, m. p. 379° (decomp.). A by-product of the oxidation is 4-*hydroxyquinoline*-3-*carboxylamide*-4-*carboxylic acid*, $OH\cdot C_9H_4N(CO_2H)\cdot CO\cdot NH_2$, faintly yellow, stout needles containing $1H_2O$ or colourless, anhydrous lamellæ, which is also obtained by hydrolysing the preceding imide with aqueous ammonia, and is the chief product when the oxidation of the trihydroxybenzonaphthyridine is effected by cold alkaline potassium permanganate (three atomic proportions of oxygen). It loses carbon dioxide at 200° or by prolonged boiling with glacial acetic acid, and is converted into 4-*hydroxyquinoline*-3-*carboxylamide* (*kynurenamide*), $OH\cdot C_9H_5N\cdot CO\cdot NH_2$, m. p. 283° (slight decomp.), which crystallises

from water or dilute acids or aqueous ammonia in colourless needles containing $1H_2O$, and from glacial acetic acid in glistening, apparently octahedral crystals containing $1C_2H_4O_2$. Kynurenamide is converted by boiling 20% hydrochloric acid or by cold nitrous acid into kynurenic acid, which yields kynurine above its m. p. or by heating with hydrochloric acid, D 1·1, at 200°. Kynurine, and also 1 : 3 : 10-trihydroxybenzo-2 : 5-naphthyridine, are oxidised to oxalylanthranilic (kynuric) acid by an excess of hot alkaline potassium permanganate.

By treatment with a hot solution of potassium hypobromite, 4-hydroxyquinoline-3-carboxylamide-2-carboxylic acid gave, not the expected 3-amino-4-hydroxyquinoline-2-carboxylic acid, but *3-bromo-4-hydroxyquinoline-2-carboxylic acid*, $C_{10}H_6O_3NBr$, yellow needles with $1H_2O$, which softens at about 120°, loses carbon dioxide at 200°, and is thereby converted into *3-bromo-4-hydroxyquinoline*, cream-coloured leaflets, m. p. 282°. C. S.

Preparation of Chloro-derivatives of *N*-Dihydro-1 : 2 : 1′ : 2′-anthraquinoneazine [Indanthrene]. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 296192; from *J. Soc. Chem. Ind.*, 1917, **36**, 591).—Indanthrene is treated with sulphur chloride in an inert medium at temperatures below 100°. The resulting dichloro-derivative is materially faster to chlorine than indanthrene blue G.C.D., and nearly as fast as indanthrene blue G.C. The product is in a finely divided state, and is suitable for the manufacture of bright-coloured pigments. H. W.

Preparation of Polychloro-substitution Products of *N*-Dihydro-1 : 2 : 1′ : 2′-anthraquinoneazine [Indanthrene]. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 296841; from *J. Soc. Chem. Ind.*, 1917, **36**, 591).—Indanthrene is suspended in an inert organic liquid and treated with an excess of chlorine at temperatures not materially exceeding 40°. The products, particularly the tri- and tetra-chloro-substitution derivatives, are characterised by their brightness of shade and resistance to the action of chlorine. H. W.

Tautomerism. The Tautomeric Reactions of 1-Phenyl-4 : 5-dihydro-1 : 2 : 4-triazole-5-one 3-Methyl Sulphone and its Salts with Diazomethane and with Alkyl Haloids. H. A. LUBS and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 950—961. Compare A., 1907, i, 258).—The sodium and silver salts of 1-phenyl-4 : 5-dihydro-1 : 2 : 4-triazole-5-one 3-methyl sulphone have been acted on by various alkyl haloids and the relative amounts of the isomeric O- and N-esters formed determined. The alkyl haloids used were methyl and ethyl iodide and allyl bromide. In all these reactions it was found that any salt and alkyl haloid in a given solvent gave a constant ratio of esters independent of the temperature and duration of the reaction, this indicating that the isomerides are formed by independent side reactions and not in accordance with the series of changes, salt $\longrightarrow$ O-ester $\longrightarrow$ N-ester, which applies

to the simple amides (compare Wheeler, A., 1903, i, 293). Any alkyl haloid gave a higher percentage of N-ester from the sodium salt than from the silver salt, and any given salt gave a higher percentage of N-ester from methyl iodide than from ethyl iodide.

[With LAWSON WILKINS.]—Allyl bromide and the silver sulphone salt gave the same ratio of esters at 25° and 100°, this case thus differing from that of silver 1-phenyl-4-methylurazole and allyl iodide, where partial conversion of the O-ester into the N-ester occurs at 100° (compare following abstract).

Diazomethane reacts with the sulphone giving the O-ester and the N-ester, the two esters being formed by reactions of the same apparent order. W. G.

The Rearrangement of 3-Allyloxy-1-phenyl-4-methylurazole. J. M. JOHNSON and S. F. ACREE (*J. Amer. Chem. Soc.*, 1917, **39**, 962—965. Compare preceding abstract).—At 60°, or below, the sodium, silver, or mercury salt of 1-phenyl-4-methylurazole each gives with allyl iodide its own ratio of N-ester and O-ester independent of the temperature and duration of the reaction. At 100°, however, in the case of the silver salt, there is a partial decomposition of the O-ester by the allyl iodide with the formation of some N-ester, the ratio thus being increased in the direction of N-ester formation W. G.

Application of Friedel and Crafts' Ketone Synthesis to Pyrazoles. A. MICHAELIS and C. A. ROJAHN (*Ber.*, 1917, **50**, 737—753).—5-Chloro-4-benzoyl-1-phenyl-3-methylpyrazole is a typical aromatic ketone, which is particularly interesting because of its behaviour towards hydrazine hydrate, whereby a dipyrazole derivative may be obtained (A., 1903, i, 288). The method originally employed for the preparation of this ketone involves several reactions and is not suited to the production of homologues, but it is now found that the Friedel and Crafts' synthesis may be applied to 5-chloro-1-phenyl-3-methylpyrazole with good results, except in the case of those derivatives of benzoyl chloride in which there are strongly electro-negative groups in the meta- or para-positions. A number of such ketones and typical derivatives, especially dipyrazoles, are now described.

The yield of 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole obtained by the new method is about 60—75% of the parent chloropyrazole.

5-*Chloro*-4-o-*chlorobenzoyl*-1-*phenyl*-3-*methylpyrazole* forms stout, highly refractive crystals, m. p. 110°, and reacts with hydrazine hydrate to give 1-*phenyl*-4-o-*chlorophenyl*-3-*methyldipyrazole*,

$$N\Big\langle\begin{matrix}NPh\cdot C\cdot NH\cdot N\\ \quad\ \| \qquad\quad \| \\ CMe\cdot C\text{———}C\cdot C_6H_4Cl\end{matrix}$$

which crystallises in silky leaflets or needles, m. p. 251°. 5-*Chloro*-4-p-*bromobenzoyl*-1-*phenyl*-3-*methylpyrazole* crystallises in colourless needles, m. p. 124°, and 1-*phenyl*-4-p-*bromophenyl*-3-*methyldipyrazole* has m. p. 246°. In the case of 5-*chloro*-4-m-*bromobenzoyl*-1-*phenyl*-3-*methylpyrazole*, m. p. 70°, the yield is exceedingly small.

5-*Chloro*-4-p-*toluoyl*-1-*phenyl*-3-*methylpyrazole* crystallises in very long needles, m. p. 86°, b. p. 220°/100 mm., and 1-*phenyl*-4-p-*tolyl*-

3-*methyldipyrazole* has m. p. 226°. The latter may be methylated to 1-*phenyl*-4-p-*tolyl*-3 : 6-*dimethyldipyrazole*,

$$N\Big\langle\begin{array}{l}NPh\cdot C\cdot NMe\cdot N \\ CMe\cdot C\text{———}C\cdot C_6H_4Me\end{array},$$

which forms long, refractive needles, m. p. 167°, and the former oxidised by means of 40% chromic acid in the cold to 5-*chloro*-4-p-*carboxybenzoyl*-1-*phenyl*-3-*methylpyrazole*, needles, m. p. 195°. This acid forms a *sodium* salt, a *silver* salt, and a *methyl* ester, m. p. 162°, and the sodium salt reacts with hydrazine hydrate at 140—150° to yield 1-*phenyl*-4-p-*carboxyphenyl*-3-*methyldipyrazole*, $N\Big\langle\begin{array}{l}NPh\cdot C\cdot NH\cdot N \\ CMe\cdot C\text{———}C\cdot C_6H_4\cdot CO_2H\end{array}$, m. p. above 300° (decomp.).

The corresponding derivatives in the ortho-series are: 5-*chloro*-4-o-*toluoyl*-1-*phenyl*-3-*methylpyrazole*, m. p. 84°, b. p. 243—245°/12 mm.; 1-*phenyl*-4-o-*tolyl*-3-*methyldipyrazole*, leaflets, m. p. 217°; 5-*chloro*-4-o-*carboxybenzoyl*-1-*phenyl*-3-*methylpyrazole* (*methyl* ester, very long needles, m. p. 122°); 1-*phenyl*-4-o-*carboxyphenyl*-3-*methyldipyrazole*, m. p. 232° (decomp.) (*hydrazide*, m. p. decomp. 233°).

Attempts were also made to obtain 4-acyl derivatives by applying the Friedel and Crafts' method to 5-chloro-3-methylpyrazole, but the only group to be attacked was the imino-group, 1-acyl compounds being formed. These are also obtained by the action of the acyl chlorides on the sodium salt of the pyrazole. 5-*Chloro*-1-*benzoyl*-3-*methylpyrazole*, $N\Big\langle\begin{array}{l}NBz\cdot CCl \\ CMe\cdot CH\end{array}$, has m. p. 36°, b. p. 302°, and the 1-*acetyl* compound, m. p. 15°, b. p. 201—202°.

5-Amino-4-benzoyl-1-phenyl-3-methylpyrazole (*loc. cit.*) forms a *hydrazone*, $N\Big\langle\begin{array}{l}NPh\cdot C\cdot NH_2 \\ CMe\cdot C\cdot CPh{:}N\cdot NH_2\end{array}$, yellow needles, m. p. 276—277°, and a dark red *dye*, m. p. 164°, when diazotised and coupled with β-naphthol. J. C. W.

Synthesis of a Naphthatetrazine from Ethyl Succinylsuccinate and Dicyanodiamide. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1917, **39**, 1011—1013).—Ethyl succinylsuccinate condenses with dicyanodiamide in aqueous sodium hydroxide to give 2 : 7-*dicyanoamino*-4 : 9-*diketotetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine*, which, like its allied compounds, is characterised by its insolubility, infusibility, and general inertness. W. G.

The Constitution of Internal Diazo-oxides (Diazophenols). II. GILBERT T. MORGAN and HENRY PHILIP TOMLINS (T., 1917, **111**, 497—506. Compare T., 1915, **107**, 657).—No authenticated case of the formation of an internal diazo-anhydride derived from a *m*-aminophenol has yet been observed. In an attempt to produce such a meta-diazo-oxide the authors have made comparative experiments on the diazotisation of 3-amino-4-hydroxy-, 3-amino-5-hydroxy-, and 2-amino-4-hydroxy-benzenesulphonic acids. The diazo-derivative of the first-named acid, namely, *benzene*-2-*diazo*-1-*oxide*-4-*sulphonic acid*, $\begin{array}{c}N_2 \\ | \\ O\end{array}\!\!>C_6H_3\cdot SO_3H$, or $\begin{array}{c}N_2 \\ O\end{array}\!\!\gg C_6H_3\cdot SO_3H$, is a yellow

solid, which has already been obtained in solution by Bennewitz (this Journ., 1874, 374), but was erroneously described as the corresponding meta-compound. 3-Amino-5-hydroxybenzenesulphonic acid gives a colourless diazo-derivative (described by Bennewitz under the belief that the parent compound contained the amino- and hydroxyl-groups in the ortho-position to one another) resembling "diazobenzenesulphonic acid" (benzene-1-diazonium-4-sulphonate); this colourless product gives rise to coloured salts with the alkali or alkaline earth metals and with organic bases such as pyridine, piperidine, dibenzylamine, or brucine, the change being represented structurally by the formulæ $OH\cdot C_6H_3<\begin{matrix}SO_3\\|\\N_2\end{matrix}$, and $\begin{matrix}N_2\\|\\O\end{matrix}>C_6H_3\cdot SO_3R$, or $\begin{matrix}N_2\\O\end{matrix}\gg C_6H_3\cdot SO_3R$, where R represents the basic radicle. 2-Amino-4-hydroxybenzenesulphonic acid also yields a colourless diazo-derivative, namely, *4-hydroxybenzene-2-diazonium-1-sulphonate*, $HO\cdot C_6H_3<\begin{matrix}SO_3\\|\\N_2\end{matrix}$; this is less stable than its isomerides and decomposes readily with liberation of nitrogen and formation of resorcinol-4-sulphonic acid, which then couples with the undecomposed portion of the diazonium compound with production of an azo-dye.

For experimental details, the original should be consulted.

D. F. T.

Product of Oxidation of *p*-Phenylenediamine (Ursol) by Hydrogen Peroxide. (Bandrowski's Base, Tetra-aminodiphenyl-*p*-azophenylene). A. HEIDUSCHKA and E. GOLDSTEIN (*Arch. Pharm.*, 1916, **254**, 584—625).—In view of the use of a solution of hydrogen peroxide and *p*-phenylenediamine as a hair-dye, the reaction between these two substances, which has been cursorily examined by Erdmann (A., 1904, i, 935), has been thoroughly studied by the authors in order to ascertain the influence on the yield of tetra-aminodiphenyl-*p*-azophenylene of the following factors: (1) concentration of the *p*-phenylenediamine; (2) amount of hydrogen peroxide (2·98% solution); (3) time of the reaction; and (4) the temperature. In all the experiments a constant amount of 10% sodium carbonate solution, which was found to have no appreciable effect on the oxidation, was added to destroy the acidic impurities in the hydrogen peroxide. In all cases, substances other than Bandrowski's base are produced in larger or smaller amounts. The theoretical yield of Bandrowski's base is calculated in accordance with the equation $3C_6H_4(NH_2)_2 + 3H_2O_2 = C_{18}H_{18}N_6 + 6H_2O$.

The influence of (1) is found by allowing aqueous solutions of *p*-phenylenediamine (1—4%) to react with 2·98% hydrogen peroxide (10% in excess of the theoretical quantity) for twenty-four hours at 18—20°. The yields of base are 6—16·3%, nothing approaching the amounts (80—90%) claimed by Erdmann ever

having been obtained. The yield does not increase proportionally to the concentration.

The influence of (2) is found by keeping the reaction mixture containing 1·88% of *p*-phenylenediamine at 18—20° for twenty-four hours. With amounts of hydrogen peroxide increasing from 0·636 mol. to 3·636 mols. (per 1 mol. of *p*-phenylenediamine), the yield of Bandrowski's base increases proportionally from 4·7% to 27·7%. With yet larger amounts of hydrogen peroxide, impure products are obtained, 5 mols. of hydrogen peroxide yielding a black, non-crystalline mass.

The effect of time is found by prolonging the period of reaction of the solutions used in the experiments under (1). After seven days, the yield of oxidation product is 30—40%, and after three months only 60%, of the theoretical.

Rise of temperature accelerates the reaction at the expense of the purity of the product, but its effect is unimportant within the range of temperature which the skin can endure.

The preceding results are represented graphically.

It has been found that *p*-phenylenediamine in solution can be estimated by precipitation as *p*-benzoquinonedichloroimide by an excess of calcium hypochlorite solution, and it is thus shown that in the preceding experiments, after removal of the Bandrowski's base, the filtrates contain 40—60% of unchanged *p*-phenylenediamine after twenty-four hours, about 50% after thirty days, and appreciable amounts after three months; in addition, about 20% of the diamine has been oxidised to unisolable products.

Despite certain differences in properties, Erdmann states (*loc. cit.*) that the base obtained by oxidising *p*-phenylenediamine with hydrogen peroxide is identical with the tetra-aminodiphenyl-*p*-azophenylene $\left[C_6H_4{<}{\begin{array}{l}N\cdot C_6H_3(NH_2)_2\\ |\\ N\cdot C_6H_3(NH_2)_2\end{array}}\right]$ obtained by Bandrowski (A., 1894, i, 236) by oxidising an ammoniacal solution of *p*-phenylenediamine by atmospheric oxygen or a solution of its hydrochloride by potassium ferricyanide. The authors prepare the base by oxidising an ammoniacal solution of *p*-phenylenediamine by aqueous potassium ferricyanide (whereby it is obtained rapidly and almost quantitatively), and find that after purification with pyridine it has m. p. 239—240° (Bandrowski gives 230—231°; Erdmann, 242—243°; Willstätter, 238—238·5°) and no water of crystallisation (compare Bandrowski and Erdmann, *loc. cit.*). The appearance of the base differs in different methods of preparation, being obtained sometimes in very slender, bronze leaflets, at other times in dark brown crystals, and yet again in large, dark red prisms. Estimations of the nitrogen by the Dumas method give the expected results; those obtained by the Kjeldahl method are 2—3% too low.

The base forms a *sulphate*, $C_{18}H_{18}N_6,2H_2SO_4$, brown powder, m. p. above 290°, and *platinichloride*, $C_{18}H_{18}N_6,2H_2PtCl_6$, blackish-grey, crystalline powder, and reacts in pyridine solution with acid anhydrides or chlorides on the water-bath to form tetra-acyl deriv-

atives; *tetrapropionyl*, red crystals, m. p. 273° (decomp.); *diphthaloyl*, brownish-red needles, m. p. 295° (decomp.); and *tetrabenzoyl*, brown crystals softening at 295°. Thioacetic acid has a simultaneous reducing and acetylating action on Bandrowski's base in pyridine solution, a colourless substance, m. p. above 300°, being obtained, which appears to be identical with Bandrowski's tetra-acetylaminodiphenyl-*p*-phenylenediamine.

Phenylcarbimide and ethyl chloroformate react normally with Bandrowski's base, yielding the *tetraphenylcarbamyl* derivative, $C_6H_4<\genfrac{}{}{0pt}{}{N\cdot C_6H_3(NH\cdot CO\cdot NHPh)_2}{N\cdot C_6H_3(NH\cdot CO\cdot NHPh)_2}$, a red powder, m. p. above 300°, and the *tetracarbethoxy*-derivative, $C_6H_4<\genfrac{}{}{0pt}{}{N\cdot C_6H_3(NH\cdot CO_2Et)_2}{N\cdot C_6H_3(NH\cdot CO_2Et)_2}$, pale red crystals, m. p. 284—285°, respectively.

The behaviour of the base towards aldehydes is very diverse. It does not react with aliphatic aldehydes. When heated on the water-bath with benzaldehyde ($1\frac{1}{2}$—2 times the theoretical amount) in pyridine solution it yields a *substance*,

$$C_6H_4<\genfrac{}{}{0pt}{}{N\cdot C_6H_3(NH\cdot CHPh\cdot OH)\cdot N:CHPh}{N\cdot C_6H_3(NH\cdot CHPh\cdot OH)\cdot N:CHPh},$$

yellow needles, m. p. 254°, which is converted at 260° into the *tetrabenzylidene* derivative, $C_6H_4<\genfrac{}{}{0pt}{}{N\cdot C_6H_3(N:CHPh)_2}{N\cdot C_6H_3(N:CHPh)_2}$, a brown powder, m. p. above 300°. *p*-Hydroxybenzaldehyde behaves in a similar manner, yielding a corresponding additive condensation *derivative*, $C_{46}H_{38}O_6N_6$, yellowish-white crystals, m. p. above 302°, but the following aldehydes yield condensation products only: cinnamaldehyde yields the *tetracinnamylidene* derivative, $C_{54}H_{42}N_6$, orange-yellow needles, m. p. 271°; anisaldehyde, the *tetra-anisylidene* derivative, $C_{50}H_{42}O_4N_6$, straw-yellow needles, m. p. above 300°, and also a *dianisylidene* derivative, $C_{34}H_{30}O_2N_6$, crimson crystals, m. p. above 300°; *p*-chlorobenzaldehyde, the *tetra-*p*-chlorobenzylidene* derivative, $C_{46}H_{30}N_6Cl_4$, colourless, crystalline powder, m. p. above 302°; vanillin, the *tetra-vanillylidene* derivative, $C_{50}H_{42}O_8N_6$, yellowish-white, crystalline powder, m. p. 301° (decomp.); and piperonal, the *tetrapiperonylidene* derivative, $C_{50}H_{34}O_8N_6$, faintly yellow leaflets, m. p. 278°, becoming brown at 255°. Bandrowski's base condenses with *p*-nitrobenzaldehyde to form the *di-*p*-nitrobenzylidene* derivative, $C_{32}H_{24}O_4N_8$, a dark red, crystalline meal, m. p. above 295°, and with salicylaldehyde, *m*-nitrobenzaldehyde, and *m*-chlorobenzaldehyde to form condensation products derived from 1 mol. of the base and 4 mols. of the aldehyde by the elimination of 3 mols. of water. These products therefore probably have the constitution $C_6H_4<\genfrac{}{}{0pt}{}{N\cdot C_6H_3(N:CHAr)\cdot NH\cdot CHAr}{N\cdot C_6H_3(N:CHAr)\cdot NH\cdot CHAr}>O$; $Ar = o\text{-}OH\cdot C_6H_4$, orange-yellow needles, m. p. above 295°; $Ar = m\text{-}NO_2\cdot C_6H_4$, yellow crystals, m. p. above 295°; and $Ar = m\text{-}C_6H_4Cl$, brown crystals, m. p. above 300°.

Bandrowski's base can be diazotised in the usual way, but the diazotised solution cannot be made to couple with amines or phenols and does not yield characteristic products by boiling.

C. S.

Transformation of ψ-Globulin into Euglobulin. W. N. BERG (*J. Agric. Research*, 1917, **8**, 449—456).—Analytical data are given which indicate the transformation of ψ-globulin into euglobulin in four serums which were heated at 60° for thirty minutes in the presence of ammonium sulphate at one-third saturation. The four serums used were two anthrax, one diphtheria, and one tetanus. In the anthrax and diphtheria serums the conversion was considerable, but in the tetanus serum it was so small as to indicate that the transformation does not take place in all serums. The use of the centrifuge was found greatly to improve the separation of the globulin precipitates from their filtrates.

W. G.

Chemistry of the Colouring Matter of the Blood. I ZALESKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1337—1653).—A complete and critical account of this subject.

T. H. P.

The Optimum Reaction in Tryptic Digestion. I. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1917, **39**, 1051—1059. Compare Michaelis and Davidsohn, A., 1911, i, 1051).—The tryptic digestion of fibrin and casein has been followed in liquids of known composition with definitely varied hydrogen-ion concentration, the range being $P_H = 2{\cdot}37$—$11{\cdot}86$. In each case there is a marked change in the hydrogen-ion concentration of the solutions on the addition of the protein. In the acid solutions the acidity is reduced, and in the alkaline solutions the alkalinity is reduced. In the case of fibrin, the equilibrium is at about $P_H = 6{\cdot}5$, and with casein at about $P_H = 4{\cdot}9$. The optimum hydrogen-ion concentration for the action of trypsin on fibrin is $C_H = 10^{-8}$ to 5×10^{-9}, and for casein 3×10^{-6} to 5×10^{-7}. Further, in the case of casein, the digestion proceeds at a degree of acidity much greater than that for the beginning of the fibrin digestion. It is probable that for each type of protein there is a distinct range for the optimum activity.

W. G.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. GERTRUD WOKER (*Ber.*, 1917, **50**, 672—677. Compare this vol., i, 62).—Polemical. A reply to Madelung (this vol., i, 285).

J. C. W.

[**Aldehyde Hypothesis of the Peroxydases.**] GERTRUD WOKER (*Ber.*, 1917, **50**, 677—679. Compare this vol., i, 61).—Polemical. A reply to van der Haar (this vol., i, 301).

J. C. W.

Tyrosinase, a Mixture of Two Enzymes. T. FOLPMERS (*Biochem. Zeitsch.*, 1916, **78**, 180—190).—Experiments are quoted which tend to show that the formation of melanin from tyrosinase

is due to two ferment actions. The first is that of a deamidase, which produces a hydroxyaldehyde from the tyrosine,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot CO_2H + O = OH\cdot C_6H_4\cdot CH_2\cdot CHO + NH_3 + CO_2.$$

The second ferment causes a further oxidation of the aldehyde (or its condensation product with ammonia) to a melanin. In the case of phenylglycine, the author succeeded in actually demonstrating the presence of a deamidase, in that he isolated benzaldehyde in the form of its *p*-nitrophenylhydrazone (m. p. 192—193°) when he treated this substance with the juice of *Euphorbia lathyris* and other plants. An analogous condensation product of *p*-nitrophenylhydrazine and aldehyde was apparently obtained when tyrosine was treated in a similar way, but not in sufficient amount for complete identification. S. B. S.

Esters of Aromatic Arsenic Compounds (*p*-Benzarsinic Acid) and Amino-acids and Higher Alcohols. ERNST SIEBURG (*Arch. Pharm.*, 1916, **254**, 224—245).—In the series $CO_2H\cdot C_6H_4\cdot AsO(OH)_2$, $CO_2H\cdot C_6H_4\cdot As(OH)_2$, $CO_2H\cdot C_6H_4\cdot AsO$, $(CO_2H\cdot C_6H_4)_2As_2$, and $CO_2H\cdot C_6H_4\cdot AsH_2$ the first, second, and fourth members are already known; the remaining two have now been prepared. *p-Benzarsine oxide* [*p-carboxyphenylarsine oxide*], $CO_2H\cdot C_6H_4\cdot AsO$, an amorphous powder which is extremely soluble in ether, is obtained by acidifying a solution of *p*-benzarsine iodide in aqueous sodium carbonate. When boiled with water, it is converted into *p*-benzarsenious acid, colourless needles, which is insoluble in ether. The oxide, which is at least ten times more poisonous than the hydrate, can be kept for at least eight days in a moderately concentrated aqueous solution of sodium hydroxide or carbonate at 0° without any appreciable diminution of its toxicity. *Phenylarsine-p-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot AsH_2$, colourless prisms, m. p. 79—80°, is prepared by reducing a methyl-alcoholic solution of *p*-benzarsinic acid with hydrochloric acid (D 1·19) and zinc dust, the product being removed by distillation with steam. In the moist state it is very sensitive to atmospheric oxygen, immediately becoming yellow and changing apparently to *p*-arsenobenzoic acid.

In connexion with his discussion (A., 1916, i, 777) of the action in the organism of preparations containing arsenic, the fact that *p*-arsenobenzoic acid injected into the animal organism is eliminated partly in the form of benzoylglycine-*p*-arsinic (hippuro-arsinic) acid is important as showing that arsenic compounds are capable of reacting in the organism under certain conditions with the degradation products of the albumin molecule. The author has now prepared and examined a number of such compounds of amino-acids and aromatic arsenic compounds.

p-Benzarsinic acid is produced almost quantitatively by heating *p*-tolylarsinic acid with nitric acid (D 1·2) for three hours at 170° in a sealed vessel. The *p*-tolylarsinic acid is conveniently prepared by the interaction of diazotised *p*-toluidine and sodium arsenite in alkaline solution. This reaction of Bart gives a very poor yield

when it is applied to the direct production of *p*-benzarsinic acid from *p*-aminobenzoic acid. *p*-Benzarsinic acid is converted by a modification of Fourneau and Oechslin's method (A., 1912, i, 928) into *p*-dichloroarsinobenzoyl chloride, which reacts with the following amino-acids in the presence of aqueous sodium hydrogen carbonate to form, after acidification of the resulting solutions, the following arsine oxides: with alanine, *benzoylalanine*-p-*arsine oxide*, $CO_2H \cdot CHMe \cdot NH \cdot CO \cdot C_6H_4 \cdot AsO$; with phenylalanine, *benzoylphenylalanine*-p-*arsine oxide*; with tyrosine, *benzoyltyrosine*-p-*arsine oxide* (in this case 2*N*-sodium hydroxide must be used instead of sodium hydrogen carbonate in order to prevent benzoylation of the hydroxyl group); with leucine, *benzoyl-leucine*-p-*arsine oxide;* with aspartic acid, *benzoylaspartic acid* p-*arsine oxide*; with glutamic acid, *benzoylglutamic acid* p-*arsine oxide*; and with pentamethylenediamine, *dibenzoylpentamethylenediamine*-pp'-*diarsine oxide*,

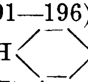
$$CH_2([CH_2]_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot AsO)_2.$$

The preceding substances are all very similar in their properties. They are amorphous, white powders which do not exhibit sharp m. p.'s, are easily soluble in methyl or ethyl alcohol and in alkali hydroxides, carbonates, or hydrogen carbonates, and do not dissolve in dilute hydrochloric acid; the oxygen of the AsO-group cannot be replaced by halogens or sulphur. They are oxidised to the corresponding arsinic acids by careful treatment with hydrogen peroxide in alkaline solution, and are reduced by sodium amalgam to arseno-compounds of the type

$$As_2(C_6H_4 \cdot CO \cdot NH \cdot CHR \cdot CO_2H)_2.$$

The latter are amorphous, yellow substances without definite m. p.'s, but the arsinic acids are crystalline: *benzoylalanine*-p-*arsinic acid*, $CO_2H \cdot CHMe \cdot NH \cdot CO \cdot C_6H_4 \cdot AsO_3H_2$, cubic crystals; *benzoylphenylalanine*-p-*arsinic acid*, needles; *benzoyltyrosine*-p-*arsinic acid*, long, pointed plates; *benzoyl-leucine*-p-*arsinic acid*, needles; *benzoylaspartic* p-*arsinic* acid, hone-shaped crystals; and *benzoylglutamic* p-*arsinic acid*, cubic crystals.

p-Dichloroarsenobenzoyl chloride reacts easily and smoothly with the higher alcohols. The reaction is effected in benzene solution in the presence of pyridine at the ordinary temperature, and finally on the water-bath. Myricyl alcohol yields *myricyl benzoate* p-*arsine oxide*, $C_{30}H_{61} \cdot O \cdot CO \cdot C_6H_4 \cdot AsO$, which in acetone solution is oxidised to the *arsinic acid*, $C_{37}H_{67}O_5As$, pointed leaflets, by hydrogen peroxide, and is reduced to the *arseno*-compound, $C_{74}H_{130}O_4As_2$, yellow powder, by phosphorous acid. Cholesterol yields *cholesteryl benzoate* p-*arsine oxide*, $C_{34}H_{48}O_3As$, colourless powder; the *arsinic acid*, $C_{34}H_{50}O_5As$, forms pointed needles, and the *arseno*-compound, $C_{68}H_{96}O_4As_2$, is a yellow powder. The arsinic acid does not give Windaus's digitonin reaction. C. S.

***p*-Sulphomethylaminophenylarsinic Acid.** J. ABELIN (*Biochem. Zeitsch.*, 1916, **78**, 191—196).—The substance, which has the constitution $SO_3H \cdot CH_2 \cdot NH$  $AsO(OH)_2$, is an *N*-substituted derivative of atoxyl. It is prepared by treating the

sodium salt of *p*-aminophenylarsinic acid with formaldehyde sodium bisulphite in concentrated solution and precipitating from this mixture the free acid with hydrochloric acid. The free acid forms needles which decompose at 148°. The substance is much less toxic than atoxyl, and its action on trypanosomes is apparently much weaker. S. B. S.

Mercuriation Products of Phenol-*p*-sulphonic Acid. E. RUPP and A. HERRMANN (*Arch. Pharm.*, 1916, **254**, 500—509).—Gautrelet states that hydrargyrol has the formula $OH\cdot C_6H_3<\begin{matrix}Hg\\|\\SO_3\end{matrix}$, is brownish-red in colour, and is soluble in water. The authors, working according to his instructions, obtained a colourless substance which is insoluble in water and is not hydrargyrol. The clear solution obtained by heating an aqueous solution of phenol-*p*-sulphonic acid with yellow mercuric oxide (1 or 2 mols.) on the water-bath soon deposits a colourless, gelatinous precipitate (the filtrate contains a small quantity of a *substance*,

$$OH\cdot C_6H_3<\begin{matrix}Hg\\|\\SO_3\end{matrix},2H_2O,$$

colourless, rhombic crystals, when 1 mol. of mercuric oxide is used), which forms a heavy, indistinctly microcrystalline powder when dried. This is 2:6-*dihydroxymercuriphenol*-p-*sulphonic acid*, $OH\cdot C_6H_2(Hg\cdot OH)_2\cdot SO_3H$, which is insoluble in water, but dissolves in concentrated aqueous sodium hydroxide, forming the *disodium* salt, $ONa\cdot C_6H_2(Hg\cdot OH)_2\cdot SO_3Na$, rhombic crystals containing $5H_2O$; from the solution carbon dioxide precipitates the *sodium* salt, $OH\cdot C_6H_2(Hg\cdot OH)_2\cdot SO_3Na$. *Sodium* 2:6-*diacetatomercuriphenol*-p-*sulphonate*, $OH\cdot C_6H_2(Hg\cdot OAc)_2\cdot SO_3Na$, colourless, microcrystalline powder, is obtained by heating a concentrated aqueous solution of sodium phenol-*p*-sulphonate with mercuric acetate on the water-bath; it readily loses acetic acid, and by prolonged boiling with water the preceding sodium salt is obtained.

Mercuric 2:6-*dihydroxymercuriphenol*-p-*sulphonate*,

$$[OH\cdot C_6H_2(Hg\cdot OH)_2\cdot SO_3]_2Hg,$$

a heavy, colourless, amorphous powder, is obtained by heating an aqueous solution of phenol-*p*-sulphonic acid with 2½ mols. of mercuric oxide or acetate on the water-bath for a long time.

Sodium 2:6-*dichloromercuriphenol*-p-*sulphonate*,

$$OH\cdot C_6H_2(HgCl)_2\cdot SO_3Na,$$

colourless needles containing $2H_2O$, is obtained (1) by adding a solution of sodium 2:6-diacetatomercuriphenol-*p*-sulphonate in aqueous sodium hydroxide to a hot solution of sodium chloride containing a moderate quantity of acetic acid; (2) by dissolving sodium 2:6-dihydroxymercuriphenol-*p*-sulphonate in hot, concentrated sodium chloride solution; (3) by heating a solution of mercuric chloride (2 mols.), sodium acetate (2 mols.), and sodium phenol-*p*-sulphonate (1 mol.) on the water-bath; and (4) by adding sodium chloride to a suspension of mercuric oxide in a solution of

sodium phenol-*p*-sulphonate. It is converted into picric acid by 20% nitric acid; into 2:6-dichloro-*p*-benzoquinone by passing chlorine into its suspension in water, and into potassium sozoiodol ($OH\cdot C_6H_2I_2\cdot SO_3K$) by warming with iodine and a solution of potassium iodide. C. S.

Physiological Chemistry.

Effect of Alcohol on the Respiration and the Gaseous Metabolism in Man. HAROLD L. HIGGINS (*J. Pharm. Exper. Ther.*, 1917, **9**, 441—472).—The author describes the effects on respiration and gaseous metabolism of the administration to men of doses of 30 c.c. and 45 c.c. of ethyl alcohol (suitably diluted with water and flavoured, but not as alcoholic beverages). An endeavour was made to secure complete rest during the experiments by carrying them out before breakfast, the men lying down and remaining as motionless as possible throughout the two to three hours' period of observation. Control experiments were made in which the flavoured water administered was free from alcohol.

In many cases the alcohol appeared to produce very little effect; in a few instances only was there a fall in the alveolar carbon dioxide tension denoting an increase in the sensitiveness of the respiratory centre. Definite actions on the bronchial muscles, affecting the "dead space," or on the heat production, as indicated by the consumption of oxygen, could not usually be detected. The rate of respiration is not altered, neither is the type of respiration changed. In half the experiments, a slight acceleration of the pulse rate occurred. The increased power of voluntary inhibition of the respiration after taking alcohol, described by Mackenzie and Hill (A., 1910, ii, 1079), is confirmed.

In the majority of cases, there is a fall in the respiratory quotient after small doses of alcohol. From the figures obtained, it is calculated that about 3·5 c.c. of alcohol per hour are oxidised in the body and the rate of oxidation is independent of the amount of alcohol taken. H. W. B.

New Method for the Estimation of the Total Volume of Blood in Man. MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 1917, **99**, 131—149).—The method consists in estimating the percentage of protein in the serum of the blood before and after the intravenous injection of 500 c.c. of physiological salt solution. If the volume of the blood is V and A and B are the percentages of protein in the serum before and after injection respectively, then $(V+500)/V=A/B$.

In its application to the human subject, the percentage of protein in the serum is estimated by means of the refractometer, and corrections are made for the effect of dilution on the refractive power

of the non-protein substances in the blood and for the volume of urine excreted by the kidney during the time occupied by the experiment.

The results are of the same order as those found by other methods. The volume of blood in normal men varies between 3300 and 5600 c.c., or 1/17 to 1/13 of the body-weight. This new method may be of clinical value, since the volume of blood of an individual is found in ordinary circumstances to vary only within small limits during periods extending over several weeks. The actual quantity of blood required for the estimations is also small, being not more than 16 c.c. H. W. B.

The Calculation of the Hydrion Concentration of the Blood from the Amount of its Free and Bound Carbon Dioxide, and the Combination of the Blood with Oxygen considered as a Function of the Hydrion Concentration. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1916, **78**, 112—144).—The first dissociation constant of carbonic acid in the presence of sodium hydrogen carbonate, $k_2 = [H^{\cdot}] \times \delta \times [Bicarb]/[CO_2]$. If 10^{-p_K} be substituted for K, then $-p_K = -p_H + \log \delta + \log . [Bicarb]/[CO_2]$, when δ = dissociation grade of the bicarbonate.

If $p_{k_1} = p_k + \log \delta$, then $p_H = p_{k_1} + \log[Bicarb]/[CO_2]$.

A series of experiments was carried out, in which the determination of p_H was made electrometrically of a known solution of sodium hydrogen carbonate in the presence of air containing varying amounts of carbon dioxide. As the absorption coefficient of water for carbon dioxide is known, the value of $[CO_2]$ at various temperatures can be calculated. An apparatus is described for saturating the bicarbonate solution with air containing carbon dioxide of known tension and for transferring the saturated liquid to the hydrogen electrode. If the value p_H is once determined for solutions with varying values of [Bicarb] and $[CO_2]$, it is, conversely, possible, by determining the amounts of free and combined carbon dioxide in a solution, to determine p_H. A similar series of experiments was carried out with blood, in which, also, the absorption coefficient for carbon dioxide is known. It was found that the determination of free and bound carbon dioxide affords a more accurate determination of the hydrion concentration than the direct electrometric measurement. It was found to be normally under 40 mm. tension of carbon dioxide $10^{-7 \cdot 33}$. Incidentally, the dissociation constant of carbonic acid was determined, and found to be greater at 38° than at 18°, which is in accordance with Julius Thomsen's thermochemical measurements. The bound carbon dioxide of the blood is exclusively in the form of a hydrogen carbonate. With diminishing carbon dioxide tensions the amount of bound carbon dioxide also diminishes, chiefly on account of the fact that oxyhæmoglobin becomes a stronger acid as the reaction becomes more alkaline. Oxyhæmoglobin (more than the other proteins), on account of its marked ampholytic character, protects the blood against changes in the hydrion concentration. This rôle is played both when acids are added or the temperature is changed,

and is of special physiological importance in that, in the circulation of the blood, as the fluid becomes more saturated with carbon dioxide, the acid action of the oxyhæmoglobin diminishes owing to its conversion into reduced hæmoglobin. The relationship established in one case by Peters and Barcroft between p_H and the constant k in Hills's formula ($y/100 = kx^{2\cdot5}/1 + kx^{2\cdot5}$, where y = percentage saturation with oxygen, x = oxygen pressure, and k varies with hydrion concentration and carbon dioxide tension) has been reinvestigated and found to hold as regards human blood in many cases. It does not hold so accurately in the cases of blood of ox, pig, and pigeon. In pregnancy, the value of the reduced p_H (that is, p_H under 40 mm. tension of carbon dioxide) is about 0·03 below the normal. S. B. S.

The Ammonia Content of Blood. V. Henriques and E. Christiansen (*Biochem. Zeitsch.*, 1916, **78**, 165—179).—By the use of a method involving the principle of that employed by Folin and Denis, the amount of ammonia in the blood from various animals was found to be about 0·27 mg. per 100 c.c. There is no marked increase in the case of the dog after a meat diet. After injection of large amounts of ammonium salts, there was an increase for a short time to about 0·9 mg., but the amount soon became normal. Neither extirpation of the kidneys nor ligature of both ureters causes an increase in the amount of ammonia in the blood. On the other hand, the amount of urea and residual nitrogen increases daily. The amino-nitrogen increases in the first day, but does not exceed about 60 mg. per 100 c.c. S. B. S.

Urea as a Source of the Ammonia in the Blood. George D. Barnett and Thomas Addis (*J. Biol. Chem.*, 1917, **30**, 41—46).—There is a marked increase in the amount of ammonia in the blood of rabbits after the administration of urea by the mouth, directly into the intestine, or intravenously. Death from ammonia poisoning frequently follows such injections. These results suggest that normally ammonia may be derived from urea in the animal organism. H. W. B.

Calcium Content of Human Blood. Henry Lyman (*J. Biol. Chem.*, 1917, **30**, 1—3. Compare this vol., ii, 271).—The amount of calcium in human blood varies but little in health and disease. The average of the analyses of fifty-three samples taken under normal and pathological conditions was 6·1 mg. of calcium per 100 c.c. of blood for the males and 7·1 mg. for females. Even in cases of advanced uræmia, where the total nitrogen was extremely high, and in those of hæmorrhage, the calcium figures were normal. H. W. B.

Residual Reducing Power of the Blood. W. Griesbach and H. Strassner (*Zeitsch. physiol. Chem.*, 1917, **99**, 224—228. Compare A., 1913, ii, 1082; Schumm, A., 1916, ii, 454).—Polemical. The authors maintain that the very small amount of so-called

residual reducing substance found by Schumm in normal blood and urine after fermentation with yeast is without significance, because it falls within the limits of experimental error of the method of estimation employed. H. W. B.

The Normal Reaction of the Intestinal Tract. J. H. LONG and FREDERICK FENGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1278—1286).—Earlier investigators of the reaction of the fluid in the small intestine have made use of the ordinary indicators; in the present investigation the hydrogen-ion concentration has been determined by electrometric measurement. Experiments were made with men, hogs, calves, lambs, and a dog, and the conclusion is drawn that in the human small intestine the reaction may vary from distinctly acid to slightly alkaline, whilst with the animals mentioned notable variations are also found, the upper portion of the intestine being most strongly acidic, whilst the lower portion may be alkaline. A considerable quantity of gas, mainly nitrogen with smaller quantities of carbon dioxide and oxygen, was found in the intestines of the hog. D. F. T.

Effect of High Temperatures on the Nutritive Value of Foods. ALBERT G. HOGAN (*J. Biol. Chem.*, 1917, **30**, 115—123. Compare A., 1916, i, 861).—The nutritive value of a protein is not impaired by heating to a high temperature in an autoclave. The deleterious effect observed when foods such as wheat and other grains are similarly subjected to heat is probably due to the destruction of indispensable accessory substances. H. W. B.

The Physiological Evaluation of the Esters of Fatty Acids. I. Ethyl Esters. JOHANNES MÜLLER and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1916, **78**, 63—96).—The experiments were carried out on a dog with the ethyl esters of the fatty acids of beef. To a dog were administered for a preliminary period a diet of meat and fat, followed by a diet in which the fat was replaced by an equivalent amount of ethyl esters, and this was followed by another period in which the original fat and meat diet was resumed. The caloric value of the ingesta and egesta was determined, and also the intake and output of carbon and nitrogen. During each period, the respiratory exchanges were determined by a Zuntz-Loewy apparatus over a period of six hours each day. The fat and unsaponifiable substances in the fæces were also estimated. The main result indicated that whereas the fat was utilised to the extent of 94%, the ethyl esters were utilised only to the extent of 75%. During the diet of the ethyl ester, there was a certain amount of degradation of body protein. Ethyl palmitate was utilised to a greater extent (75%) than the stearate (64%). It is claimed that ethyl esters can be used to replace fats in a war diet. S. B. S.

Supplementary Dietary Relationship between Leaf and Seed as Contrasted with Combinations of Seed with Seed. E. V. MCCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1917, **30**, 13—32.)—The results of these experiments on rats indicate that

it is difficult, if not impossible, to obtain even a moderate amount of growth over an extended period on a diet restricted to the seeds of plants, because of their inadequate content of salts, particularly of sodium and calcium. The leaf, however, contains a large proportion of salts and is especially rich in salts of sodium and calcium. Mixtures of leaf and seed are therefore more efficient than mixtures of seeds as a diet for growing animals. Moreover, the leaves of some plants, lucerne, for example, are several times richer in "fat-soluble A" than are the wheat, oat, and maize kernels. Certain small seeds, such as flax and millet seed, have approximately the same value as the leaf in this respect, and when incorporated with inorganic salts in sufficient amount with wheat, oats, or maize constitute a diet which is adequate to meet the needs of the growing animal. H. W. B.

The Effect of the Ingestion of Aluminium on the Growth of the Young. J. T. LEARY and S. H. SHEIB (*J. Amer. Chem. Soc.*, 1917, **39**, 1066—1073. Compare Kahn, *Biochem. Bull.*, 1911, **1**, 235, and Steele, *Amer. J. Physiol.*, 1911, **28**, 94).—Aluminium, when added in the form of aluminium hydroxide to the diet of young puppies, caused a marked increase in the fæcal phosphates and a decrease in the amount excreted in the urine, accompanied by a decrease in the urinary acidity. There was also a decrease in the nutritional value of the diet when aluminium was added to it. The addition of aluminium hydroxide in varying amounts to the diet of young rats appeared to have no great effect on their growth, an ill-effect only being observed in one case. Absorption of aluminium occurred with the dogs and the rats, the liver being the seat of the greatest deposition. W. G.

Mechanism of Cytolysis in Echinoderm Eggs. II. A. R. MOORE (*J. Biol. Chem.*, 1917, **30**, 5—11. Compare this vol., i, 185).—The experiments carried out with eggs of the sea-urchin (*loc. cit.*) have been repeated with those of the starfish, *Asterias forbesii.* The graphs derived from the experimental results indicate that the rate of cytolysis of starfish eggs is not constant, but depends on the chemical state of the egg, which in turn is determined by the age of the egg or the extent to which certain oxidations have taken place in it.

Treatment of starfish eggs with isotonic solutions of the chlorides of barium, strontium, calcium, and magnesium does not accelerate the rate of cytolysis in the manner observed with sea-urchin eggs. On the contrary, a slight inhibitory action is observed in each case. H. W. B.

Genesis of Carbamide. I. Can Muscular Tissue Generate Carbamide? UGO LOMBROSO (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 569—573).—Blood circulating in functioning muscular tissue may undergo a marked increase in its content of carbamide. The addition of amino-acids does not constitute a necessary or even favourable condition for such increase; indeed, in some instances

in which a large proportion of amino-acid was added to the blood and a considerable percentage of it disappeared during the circulation, no increase of carbamide was observed. The greatest increase in the amount of carbamide in the blood was obtained when the muscular tissue and the blood employed were taken from a dog previously fed with meat. T. H. P.

Biochemistry of Silicic Acid. MAX GONNERMANN (*Zeitsch. physiol. Chem.*, 1917, **99**, 255—296).—Silica is present in most tissues. The quantities, expressed in percentages of the total ash, are as follows: hair, 2 to 30; milk, 0·3 to 0·4; thymus, 8; adrenals, 7 to 16; blood corpuscles, 3; serum, 2 to 3; fibrin, 15 to 30; muscle, 2 to 4; intestine, 2 to 13. The author considers that silica is absorbed in the duodenum and excreted into the large intestine like iron compounds and other substances.

It appears that good effects have been observed to follow the administration of silicic acid in cases of tuberculosis. Most herbs contain considerable quantities of silica, and it is found on analysis that those herbs which are used by the country folk of Middle Europe for the cure of tuberculosis contain the largest percentages of silica. H. W. B.

Concentration of Dextrose in the Tissues of Normal and Diabetic Animals. WALTER W. PALMER (*J. Biol. Chem.*, 1917, **30**, 79—114).—The author has estimated the concentration of dextrose in the muscle, liver, heart, kidney, spleen, pancreas, stomach, intestine, skin, lung, and eye tissues of normal and diabetic dogs and rabbits, under varying conditions. In a few instances the dextrose has been estimated in the bladder, parotid glands, œsophagus, uterus, tongue, diaphragm, thyroid, aorta, trachea, and brain. The tissues are removed as rapidly as possible from the body, and, after weighing, treated with boiling water to arrest enzymic action. The proteins are removed from the aqueous extract by colloidal iron and the dextrose estimated by Benedict's method.

The concentration of dextrose in the tissues is found to bear a more or less constant relation to the amount of sugar in the blood. It is invariably lower than the concentration of sugar in the blood, except in the liver, where the higher concentrations may be probably explained by rapid glycogenolysis. The largest amounts of sugar are found in the liver, the smallest quantity in the brain, the difference being largely accounted for by difference in vascularity. In the muscles the amount of dextrose is low, varying in normal animals between 0·04% when the dextrose in the blood is 0·10% and 0·41% when the dextrose in the blood reaches 1·05% after the intravenous injection of dextrose; whilst in diabetic animals it falls within the normal limits, even although the hyperglycæmia rises as high as 1·43%. The amount of dextrose found in either normal or diabetic tissues during hyperglycæmia is not influenced by variations in the method of producing the hyperglycæmia.

The chief difference in the results obtained from normal and

diabetic animals respectively is observed in the figures for the concentration of dextrose in striated muscle, which are invariably higher in the former class when the amount of dextrose in the blood is the same in both classes. The significance of this difference is not apparent. H. W. B.

Human Adipocere. R. F. RUTTAN (*Trans. Roy. Soc. Canada*, 1917, [iii], **10**, 169—170. Compare Ruttan and Marshall, this vol., i, 364).—The author has analysed specimens of adipocere of human origin, some of which were dry and firm and others soft and oily. The latter consist of immature adipocere and differ from the waxy variety in containing more oleic acid, proteins (soft connective-tissue and hyaline muscular fibres), and calcium soaps.

Human adipocere, whether mature or immature, shows a remarkable similarity in composition to the adipocere from the pig (*loc. cit.*). It is essentially composed of saturated fatty acids, glycerides being present in traces only. The two isomeric monohydroxystearic acids derived from oleic acid are invariably present, and the disappearance of unaltered oleic acid marks the final stage in the formation of mature adipocere.

Adipocere is regarded as the product of the hydrolysis of fats by water where the time factor and the concentration of the reacting water are almost indefinitely great and where the soluble product, glycerol, is rapidly removed. Bacterial and enzymic actions play a quite secondary part in the production of adipocere. The hard, waxy character of the mature substance is largely due to the presence of the two hydroxystearic acids. H. W. B.

Comparative Investigations on the Excretion of Arsenic in Human Urine after Injection of Various Arsenical Medicaments. GEORG LOCKEMANN (*Biochem. Zeitsch.*, 1916, **78**, 1—36).—As regards the rate of elimination of arsenic, the medicaments can be divided into two classes. In the first, which includes atoxyl and arsacetin, the greater part of the arsenic is excreted in the first two days after injection. The second class includes salvarsan, neosalvarsan, and arsenophenylglycine, and, after injection of these substances, arsenic is excreted only very slowly. There are differences in the rate of excretion of the various medicaments by male and female. Arsacetin is slightly degraded in the passage through the body, there being partial scission of the acetyl group with formation of atoxyl, and there is also a partial scission of the arsenic group. The substances containing the free amino-group were isolated by conversion into the diazo-derivative and the coupling of this with naphthylamine; the arsenic was estimated in the precipitate thus formed. The excretion of arsenic, both in male and female, follows a periodic course, more being excreted in the first, third, fifth day, etc., than in the intervening days. The rate of excretion diminishes after repeated doses. Particulars are given in detail as to the amounts of arsenic excreted at various intervals after various methods of injection (intramuscular, intravenous, and subcutaneous). S. B. S.

Influence of the Protein Intake on the Excretion of Creatine in Man. W. DENIS [with ANNA S. MINOT] (*J. Biol. Chem.*, 1917, **30**, 47—51).—In five cases of Grave's disease it is shown that the amount of creatine excreted by these individuals is dependent on the intake of protein, being increased by high protein feeding and decreased or even eliminated by low protein feeding. It is suggested that a certain fraction of the ingested protein is transformed into creatine, transported to the muscles, and there absorbed. If so much creatine is manufactured that the muscles become supersaturated, creatine is excreted by way of the kidney. What constitutes supersaturation depends not only on the total mass of muscle, but on the capacity for creatine absorption possessed by those muscles. In childhood, in Grave's disease, and in other pathological conditions, the saturation point of the muscle for creatine is probably lower than in the normal person.

H. W. B.

Theory of Diabetes. VIII. Timed Intravenous Injections of Dextrose at Lower Rates. W. D. SANSUM and R. T. WOODYATT (*J. Biol. Chem.*, 1917, **30**, 155—173).—The authors describe experiments which indicate that the maximum rate at which dextrose can be continuously administered by intravenous injection to normal resting rabbits and dogs without causing gross glycosuria is about 0·85 gram per kilo. of body-weight per hour. This is termed the normal intravenous dextrose toleration limit. Within rather wide limits, the water administered simultaneously with the dextrose may be varied without appreciably affecting the rate of utilisation of the dextrose. Continued intravenous injection of dextrose at uniform rates between 0·9 and 2 grams per kilo. per hour leads to continued excretion of dextrose in the urine, also at uniform rates. The ratio of the intake to the output rate differs with different individuals. When the rate of injection is 1·8 to 2 grams per kilo. per hour, the excretion of dextrose per hour varies in different individuals from 2 to 10%. of the amount injected. For any individual case the rate at which dextrose enters the blood determines the rate of utilisation and excretion of dextrose, regardless of the volume of the blood and urine or the concentration of dextrose in them.

H. W. B.

Formation of Lactic Acid and Acetoacetic Acid in the Livers of Diabetic Animals. G. EMBDEN and S. ISAAC (*Zeitsch. physiol. Chem.*, 1917, **99**, 297—321).—When dextrose is mixed with blood and perfused through the liver of a dog, it is transformed in part into lactic acid (Embden and Kraus, A., 1912, ii, 1070). The authors now find that similar perfusion of the liver of a depancreatised dog does not yield any lactic acid. Similar results are obtained with lævulose, although in a few cases small amounts of lactic acid are formed. When the diabetes is produced by phloridzin, the liver exerts a similar action, but in some cases dextrose is also partly converted into lactic acid. The livers of diabetic animals therefore fail to convert the simple carbohydrates into lactic acid,

but instead transform them into acetoacetic acid. In the experiments described by the authors it is noted that the amounts of lactic and acetoacetic acids produced vary inversely the one with the other. H. W. B.

Identification of the Pentose in a Case of Pentosuria. Alma Hiller (*J. Biol. Chem.*, 1917, **30**, 129—134).—The melting point .and mutarotation of the osazone prepared from the pentose in the urine in a case of pentosuria indicated the presence of *d*-xylose or a closely related pentose. The rotation of the concentrated urine excluded *d*-xylose, whilst the presence of a ketose was indicated by the bromine and colour tests. The pentose is therefore probably *d*-xyloketose. H. W. B.

Reaction of Sera as a Factor in the Successful Concentration of Anti-toxic Sera by the Methods at Present in Use. Annie Homer (*Biochem. J.*, 1917, **11**, 21—39. Compare A., 1916, i, 614).—The author directs attention to the importance of controlling the reaction of an anti-toxic serum during the processes generally employed in its concentration. On the reaction of the serum depends not only the extent of the heat denaturation of the proteins of the serum, but also the successful precipitation of these proteins by ammonium sulphate. Unless the reaction is regulated, the necessary increased precipitation of the proteins cannot be ensured except by the addition to the serum of phenol, ether, chloroform, or similar substance which favours the destruction of antitoxin. H. W. B.

The Astringent Action of Aluminium Salts, especially of the Formate. A. Loewy and R. Wolffenstein (*Biochem. Zeitsch.*, 1916, **78**, 97—111).—Experiments are described which indicate the advantages of the use of the formate of aluminium as compared with the acetate. The former preparation is less irritant. It is best employed in solution which contains some sodium sulphate. Such a solution readily precipitates proteins and also produces contraction of the blood vessels. S. B. S.

Inhibition of Digestion of Proteins by Adsorbed Tin. B. C. Goss (*J. Biol. Chem.*, 1917, **30**, 53—60).—Tin is readily adsorbed from solutions by coagulated proteins in amounts varying with the concentration according to the adsorption law of Freundlich. This adsorption takes place rapidly at first, and then continues to increase slowly for several days, presumably because of the time required for diffusion into the solid. The adsorption complex is extremely stable, and does not lose tin to a dilute acid or alkaline aqueous phase containing no tin, although the amount of tin in the solid may be as high as 50%. The presence of this tin, even in small amounts, interferes with the digestion of the protein by either pepsin or trypsin, but after a time solution of nearly all the protein occurs and only a small residue remains, which contains practically all the tin. It appears from these observations that it is only a part

of the protein, directly joined to the tin, of which the digestion is hindered, so that the effect of this retardation on the physiological value of tinned foods is probably small, since the total tin in such foods rarely exceeds 0·03%.

Prolonged digestion of the tin–protein complex with pepsin or trypsin does not lead to the solution of the tin. The activity of the enzymes also remains unimpaired, even after being one hundred hours in contact with the tin–protein complex. It is probable, therefore, that the tin present in canned foods escapes digestion and absorption in the animal body, and is therefore devoid of toxic action. H. W. B.

Olfactology of the Methylbenzene Series. E. L. BACKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 943—956).—A comparison has been made of the smallest quantities of benzene, toluene, xylene, ψ-cumene, and durene which can be detected by the olfactory organ. The quantity diminishes as the number of substituent methyl groups increases. The electrical charge produced by spraying equimolecular aqueous solutions of the above substances increases from benzene to xylene, and then diminishes for the higher homologues. Experiments on the olfactory properties of mixtures afford indications of compensation effects.
H. M. D.

Purine Metabolism after Poisons. JULIUS POHL (*Biochem. Zeitsch.*, 1916, **78**, 200—223).—The allantoin and uric acid output after administration (to rabbits or dogs) of the following substances was investigated: sodium chloride, bromide and iodide, calcium chloride, arsenious acid, lead carbonate, sodium malonate, sodium cyanide, benzene, bromobenzene, salicylic acid, sodium phenylcinchonate (alophan), pilocarpine, morphine, quinine, colchicine, adrenaline (*l* and *r*), thyroid gland. Increased output followed administration of arsenic, lead, sodium cyanide, bromobenzene, morphine (in all these cases of allantoin), colchicine (of uric acid), and adrenaline (of allantoin and uric acid).
S. B. S.

Chemistry of Vegetable Physiology and Agriculture

Decomposition of Protein Substances through the Action of Bacteria. R. H. Robinson and H. V. Tartar (*J. Biol. Chem.*, 1917, **30**, 135—144).—The authors have studied the chemical changes that occur when a protein is acted on by certain organisms, *B. subtilis*, *B. mycoides*, and *B. vulgaris*, present in most soils. The percentages of nitrogen combined in various forms are estimated before and after bacterial action by Van Slyke's method.

The results indicate that all the forms in which nitrogen is combined are changed more or less by the action of the bacteria, and the end-product ammonia is formed. The monoamino-acid nitrogen and diamino-acid nitrogen of the protein are the chief sources of the ammonia produced, but the action of the bacteria is not confined to one particular form to the exclusion of the others. The rapidity of action varies greatly with different proteins, casein showing no further change after a few days, whilst gliadin continues to evolve ammonia after thirty days. The reason for the arrest of bacterial action has not been elucidated; it does not appear to be the formation of a toxic substance.

The changes observed indicate that the bacterial decomposition of proteins is effected by hydrolysis with the formation of the amino-acids and subsequent degradation with the liberation of ammonia. H. W. B.

New Type of Chemical Change Produced by Bacteria. Conversion of Histidine into Urocanic Acid by Bacteria of the Coli-typhosus Group. HAROLD RAISTRICK (*Biochem. J.*, 1917, **11**, 71—77).—Histidine is converted into urocanic acid (β-iminoazolylacrylic acid) in a medium consisting of Ringer's solution and histidine, by the following bacteria: *B. coli communis*, *B. typhosus*, *B. paratyphosus*, *B. enteritidis*, and *B. dysenteriae*. The change is represented by the equation $C_3H_3N_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H = C_3H_3N_2{\cdot}CH{:}CH{\cdot}CO_2H + NH_3$. H. W. B.

The Chemistry of the Fats of Tubercle Bacilli. MAX BÜRGER (*Biochem. Zeitsch.*, 1916, **78**, 155—164).—Tubercle bacilli contain "cerolipoids" consisting partly of the homologous fatty acids of the series $C_nH_{2n}O_2$ from lauric to palmitic acids, and partly of high molecular alcohols of the formula $C_nH_{2n-2}O$ ($C_{15}H_{28}O$, $C_{19}H_{36}O$, and $C_{29}H_{56}O$). S. B. S.

Chemical Conditions for the Development of the Reproductive Organs in some Yeasts. KENDO SAITO (*J. Coll. Sci. Imp. Univ. Tokyo*, 1916, **39**, (3), 1—73).—The author has ascertained the action of various chemical agents on the development of spores by the following three yeasts: *Zygosaccharomycetes manchuricus*, *Schizosaccharomycetes octosporus*, and *Saccharomycetes manchuricus*. The results indicate that the formation of spores only occurs when the medium in which the yeast cell is grown contains members of definite classes of substances.

Cells of *Zygosaccharomycetes*, when transferred to pure water, do not form spores. If, however, a carbohydrate or similar substance is present, spores are formed, and this formation of spores occurs more readily in the presence of a simple monosaccharide than of a polysaccharide or carbohydrate derivative, such as dulcitol. The addition of a trace of potassium phosphate and Witte's peptone accelerates the production of spores. Ammonium salts, amino- and weak organic acids inhibit the reproductive process.

The concentration of the medium may be varied within wide limits without entirely arresting the development of spores. Thus, highly concentrated solutions up to 25% of potassium nitrate do not inhibit spore formation as much as an isotonic sodium chloride solution. The extreme limits of concentration applicable vary according to the previous training as regards food of the particular yeast employed, since yeasts, like bacteria and fungi, show adaptative capacity and may be gradually accustomed to unfamiliar circumstances.

Most yeasts require the withdrawal of food before spore formation can ensue. Schizosaccharomycetes is an exception to this rule, inasmuch as reproduction in this manner occurs in the unchanged medium, provided other conditions, such as temperature and degree of oxygenation, are favourable. H. W. B.

The Proteoclastic Ferments of Yeast and their Relationship to Autolysis. K. G. Dernby (*Biochem. Zeitsch.*, 1917, **81**, 109—208).—The author confirms the fact, originally discovered by Vines, that yeast contains more than one distinct proteoclastic ferment. He has succeeded in demonstrating the presence of three, which are analogous to, but differ in certain particulars from, the proteoclastic ferments of the animal organism. These ferments are: I. Yeast pepsin, which can degrade genuine proteins to peptones (but not further). Its optimal action is in a medium of $p_H=4—4{\cdot}5$, whereas the animal pepsin acts best in a medium of $p_H=1{\cdot}5$ (Sörensen). II. A yeast tryptase, which does not act on the proteins of yeast, but can degrade certain proteins, such as acid albumin, gelatin, caseinogen, into peptides and amino-acids. Its optimal action is in a medium of $p_H=7$, as compared with that of $p_H=8$, which is optimal for animal tryptase. III. A yeast ereptase, which readily degrades peptones and polypeptides into amino-acids and has an optimal action in a medium of $p_H=7{\cdot}8$, which is very nearly the same as that of animal ereptase. It differs, however, from the latter in that its action is not markedly inhibited by neutral salts, whereas the animal ereptase is. A concentration of $0{\cdot}5N$-salt solution has little action on yeast ereptase, whereas the animal ereptase is inhibited by a concentration of $0{\cdot}02N$. The individual ions have apparently little action, as they act more or less alike, the diminution of the action of the ferment being controlled by the salt molecules as a whole. The autolysis of yeast is due to the successive action of the various ferments, and the maximal action takes place in a medium of $p_H=6{\cdot}0$, which is midway between the optimal p_H concentrations for the yeast pepsin and the tryptase. Deamidases play only a subordinate rôle in the autolysis.

The method of investigation employed by the author consisted in following the course of degradation of yeast and other products in media with varying hydrogen-ion concentrations, both in the presence and absence of buffer solutions. In the absence of such solutions, the hydrion concentration changed during the course of the ferment action. The chief indication as to the presence of

various ferments was afforded in this case by estimating the total nitrogen, amino-peptide, and protein nitrogen in solutions of the autolysis mixture after varying intervals of autolysis. When no buffer mixture was present, the total nitrogen and amino-nitrogen continually increased, especially towards the end, whereas the peptide nitrogen first increased and then diminished, and the protein nitrogen first diminished (slightly) and then increased (slightly). The p_H changed during the reaction from 6·0 to 6·8. The results indicate that at the commencement the pepsin was chiefly active, whereas towards the end, in the more alkaline medium, the erepsin was most active.

The detailed action of the various ferments was also investigated by extracting them from yeast plasmolysed by chloroform in presence of calcium carbonate and submitting the extracts to dialysis against diminished pressure by a method recently described by Sörensen. The action of the pepsin was investigated on acid albumin by Sörensen's method, the unchanged protein being precipitated by Schjerning's stannous chloride solution, and also by the thymol–gelatin method of Palitzsch and Walbum (A., 1913, i, 112). The adaptation of this method is described in detail, and the fact that it indicated the presence of two optima of proteoclastic activity showed the presence of two ferments (tryptase and erepsin). The action of the erepsin on glycylglycine was investigated in detail and compared with that of animal erepsin. The reaction in the presence of a buffer mixture (phosphates) is unimolecular. S. B. S.

The Presence of Emulsin-like Ferments Separable from the Cells of Bottom Yeast, and the Absence of Myrosin in Berlin Top and Bottom Yeast. CARL NEUBERG and EDUARD FÄRBER (*Biochem. Zeitsch.*, 1916, **78**, 264—272).—The maceration juice of bottom yeast contains all three ferments which act on amygdalin (amygdalase, prunase, and oxynitrilase). β-Glucosides are also hydrolysed by the maceration juice of Munich bottom yeast. The myrosin ferment has been found neither in top nor bottom yeasts (free yeast and maceration juice of dried cells) of Berlin, and is also absent in dried Munich bottom yeast. S. B. S.

Conditions of Activation of Washed Zymin and the Specific Function of Certain Cations in Alcoholic Fermentation. ARTHUR HARDEN (*Biochem. J.*, 1917, **11**, 64—70).—Zymin and dried yeast, which have been inactivated by washing, can be activated by the addition of a pyruvate or acetaldehyde in the presence of dipotassium hydrogen phosphate. The potassium salt may be replaced by diammonium hydrogen phosphate, but not by the corresponding sodium salt. A specific difference in relation to alcoholic fermentation exists therefore between the ions of sodium on the one hand and of potassium and ammonium on the other. The presence of phosphate is also essential if activation is to occur.

These results appear to support the view that acetaldehyde is an intermediate product in alcoholic fermentation, and is reduced in

that process to alcohol by hydrogen liberated at a previous stage of the decomposition. H. W. B.

The Course of Alcoholic Fermentation in an Alkaline Medium. I. Cell-free Fermentation in Alkaline Solutions. CARL NEUBERG and EDUARD FÄRBER (*Biochem. Zeitsch.*, 1916, **78**, 238—263).—In order to throw further light on the stages of alcoholic fermentation, experiments were carried out on the fermentation processes under atypical conditions. Normally, alcoholic fermentation takes place in an acid medium. It has been found by the authors that it will also take place in fairly strong alkaline media, provided that the alkali is added after fermentation has commenced. If it is added at the start, a precipitate is produced and fermentation is inhibited at low concentrations. This precipitate does not form in the presence of even larger amounts of alkali if the latter is added after once the fermentation has commenced. The experiments were carried out with maceration juice prepared from dried yeast, and the alkalis used were potassium and sodium carbonates, sodium sulphite, potassium metaborate, and potassium phosphate. Full fermentation took place in concentrations of 0·1 to 0·2*M* solutions of all these except the sulphite, with which a concentration of more than 0·02*M* was inhibitory in its action when these were added directly to the fermentation mixture. If the alkalis are added to the mixture after fermentation has started, the amounts tolerated are much higher (0·25—0·35*M* of the carbonates, etc., and 0·04—0·05 of sulphite). Experiments indicate that addition of alkalis to fermentation mixtures at the start do not exert their inhibitory action owing to removal of phosphates. Preliminary experiments indicate also that the products of fermentation in alkaline solution are not the same as the normal. S. B. S.

Amygdalin as Nutriment for Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 922—927).—Earlier observations have shown that amygdalin is resolved into dextrose, benzaldehyde, and hydrogen cyanide by the extract from the cells of *Aspergillus niger*. This does not occur with the living cells, and in these circumstances the amygdalin is absorbed and assimilated by the mould which multiplies in the amygdalin solution. The experiments now described show that the organism will not develop if any considerable proportion of the amygdalin is already hydrolysed. The retardation is mainly due to the benzaldehyde, the action of which is possibly due to its ready solubility in fats and on the other hand to its rapid oxidation to benzoic acid. The behaviour of amygdalin and its products of hydrolysis towards the cells of *Aspergillus niger* affords an indication of a general method for the introduction of narcotic substances into living organisms. H. M. D.

Spontaneous Infection of a Saturated Potassium Chlorate Solution. H. J. WATERMAN (*Chem. Weekblad*, 1917, **14**, 514—515).—An account of a saturated solution of potassium chlorate which

did not crystallise, but after several weeks developed an unknown mould of the *Penicillium* type with green spores, and a red ferment.

A. J. W.

The Formation of Starch-like Substances by Moulds. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1917, **81**, 80—86. Compare this vol., i, 370).—In the presence of mineral acids, *Aspergillus niger* can produce in the culture medium a substance giving the blue iodine reaction from glycerol and mannitol. It can also produce such a substance in fairly high concentrations from the following organic acids (the reaction being the most intense in the first-named acids) when they are used as the source of carbon in the medium: tartaric, citric, malic, succinic, and oxalic acids. The substance producing the iodine reaction tends to disappear after a certain interval.

S. B. S.

Utilisation of Certain Pentoses and Compounds of Pentoses by Glomerella cingulata. L. A. HAWKINS (*Amer. J. Botany*, 1915, **2**, 375—388; from *J. Soc. Chem. Ind.*, 1917, **36**, 663).—Previous investigators have shown that pentoses and pentosans are of some value as food for higher animals, but the latter appear to secrete no enzyme capable of hydrolysing pentosans, this transformation being probably effected by intestinal bacteria. Some of the invertebrates utilise pentoses readily, and can probably hydrolyse some pentosans. Pentoses have been found to be a good source of carbon for certain fungi, and there is evidence of decomposition of pentosans by enzymes secreted by fungi, although the products of such decomposition have apparently not been identified. In experiments with *Glomerella cingulata*, the author has found that this fungus can utilise dextrose, xylose, arabinose, xylan, or arabin as sole source of carbon. The three sugars are most efficiently utilised, xylose perhaps best of all. The pentosans are much less readily assimilated, and arabin less readily than xylan. The presence of a pentosanase in filtered aqueous extracts of the fungus mycelium was also demonstrated by the conversion of xylan into xylose, the latter being isolated in the crystalline form.

H. W.

Accessory Factors for Plant Growth. OTTO ROSENHEIM (*Biochem. J.*, 1917, **11**, 7—10).—An aqueous extract of Bottomley's bacterialised peat has remarkable growth-stimulating properties, which cannot be ascribed to the manurial value of the small amounts of nitrogenous and other substances present in it. The author suggests that the effect produced on plant growth is due to a substance or substances analogous to the vitamines or accessory substances in animal growth. Alcoholic or aqueous extracts of the treated peat give a precipitate with phosphotungstic acid, whilst similar extracts of ordinary peat or garden soil give only a faint opalescence or remain clear. The positive outfall of certain colour tests also indicates the presence of a substance similar to a vitamine in the treated peat.

H. W. B.

Influence of Manganese taken up by Plants on their Composition. PAUL EHRENBERG and OTTO NOLTE (*Landw. Versuchs-Stat.*, 1917, **90**, 139—145).—Direct experiment shows that increase of the manganese-content of plants to 0·1% produces no certain appreciable change in the composition of the incombustible matter of the plants. T. H. P.

Viscosimetry of Living Protoplasm. FRIEDL WEBER (*Kolloid Zeitsch.*, 1917, **20**, 169—173).—A discussion of the methods which have been used in the determination of the viscosity of living protoplasm and of the factors which influence the magnitude of the viscosity. H. M. D.

Formation of Starch [in Plants exposed] in the Spectrum. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1917, **35**, 44—69).—The author has investigated the formation of starch in the leaves of *Phaseolus multiflorus, Impatiens, Tropaeolum,* and *Coleus* at different positions of the spectra of the sun, moon, and various electric lamps. The extreme limits of wave-length within which starch is formed are found to be 760 and 330 $\mu\mu$. The latter value may be somewhat higher than the true minimum, since the experiments were made in the autumn, whereas June is the most suitable month. The region of starch-formation depends to some extent on the length of the exposure and on the nature of the source of light. The curves connecting the amount of starch formed with the wave-length exhibit a principal maximum and one or two subsidiary maxima. T. H. P.

Deamidisation. KARL SCHWEITZER (*Biochem. Zeitsch.*, 1916, **78**, 37—45).—By means of the tyrosinase from potatoes, glycine can be degraded according to the equation $NH_2 \cdot CH_2 \cdot CO_2H + O = H \cdot CHO + NH_3 + CO_2$. The reaction takes place in the presence of an alkali (preferably calcium hydroxide), or of solutions of *p*-cresol; chlorophyll appears to accelerate the reaction. Formaldehyde could be detected in green leaves which had been exposed to the light, but not in those exposed to the dark, but this fact does not necessarily imply that the Baeyer hypothesis as to the formation of formaldehyde from carbon dioxide is correct, as the aldehyde can be the product of photochemical decomposition of other products. The results indicate that the existence of a deaminase is not proven. S. B. S.

The Protein Content of Variegated Leaves Investigated by Molisch's Macroscopic Method. GEORG LAKON (*Biochem. Zeitsch.*, 1916, **78**, 145—154).—According to Molisch, the presence of proteins can be demonstrated in leaves which have been treated with hot water and then alcohol by means of the biuret, xanthoproteic, and Millon reagents. This method has been applied by the author with many leaves, especially the variegated leaves of *Acer negundo.* The green parts give marked protein reactions,

whereas the white parts remain almost uncoloured. The chromatophores appear to contain, therefore, the greatest amounts of protein. In this respect, Molisch's conclusions are confirmed.
S. B. S.

Proteins of the Peanut, Arachis hypogœa. II. Distribution of the Basic Nitrogen in the Globulins Arachin and Conarachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1917, **30**, 33—38. Compare this vol., i, 191).—The globulins of the peanut contain the basic amino-acids, arginine, histidine and lysine and cysteine. Arachin contains 5% and conarachin 6% of lysine. The relatively high percentage of lysine in the proteins of the peanut suggests that this seed might be used to advantage in supplementing diets deficient in lysine.
H. W. B.

Substance accompanying Lapachol in Greenheart Wood. O. A. OESTERLE (*Arch. Pharm.*, 1916, **254**, 346—348).—The author has isolated from the greenheart wood of *Bignonia leucoxylon*, in addition to lapachol, a very small quantity of a *substance*, $C_{29}H_{26}O_4$, colourless needles, m. p. 222—223°, darkening at 215°, which is not volatile with steam, is insoluble in alkali hydroxides or carbonates, and develops a bluish-violet coloration with concentrated sulphuric acid. It is certainly not lapachonone, which not infrequently accompanies lapachol in woods. C. S.

Microchemistry of Plants. IV. Organic Lime-balls and Siliceous Bodies in Capparis. HANS MOLISCH (*Ber., Deut. bot. Ges.*, 1916, **34**, 154—160).—Almost every parenchymatous cell of the leaf-stem of *Capparis callosa* contains a spherical, colourless, highly refractive body, which is found to be an organic calcium compound, possibly a double malate of calcium and magnesium. Bodies containing silicic acid and an organic substance are also present. These two bodies are also found in the leaf itself and in the stem of the plant. T. H. P.

Plant Food Materials in the Leaves of Forest Trees. PAUL SEREX, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 1286—1296). —The leaves of the chestnut (*Castanea Dentata*), the sugar maple (*Acer saccharum*), and white oak (*Quercus alba*) were gathered in spring and autumn from apparently healthy specimens on different types of soil, and were examined as to their content of phosphorus, potassium, and nitrogen. The spring leaves contained a higher proportion of nitrogen and potassium than the autumn leaves from the same trees, whilst the percentage of phosphorus varied with the species and the section of the tree from which the leaves were obtained. The content of nitrogen, phosphorus, and potassium was higher in leaves from trees on a loam soil than from those on clay soil; with the maple and oak the percentage of these elements was generally higher in leaves from the upper branches, whereas with the chestnut the reverse appeared to be the case. D. F. T.

Anatomy and Chemism of the Lichen, Chrysothrix nolitangere. EMANUEL SENFT (*Ber. Deut. bot. Ges.*, 1916, **34**, 592—600).—This lichen seems to owe its yellow colour only to the calycin present. T. H. P.

Raffinose in the Seed of the Jute Plant (Corchorus capsularis). HAROLD EDWARD ANNETT (*Biochem. J.*, 1917, **11**, 1—6).—The seeds of the jute plant contain between 2% and 3% of raffinose. H. W. B.

Microchemistry of Droseraceæ. M. FÜNFSTÜCK and R. BRAUN (*Ber. Deut. bot. Ges.*, 1916, **34**, 160—168).—The root and leaf-stems of *Drosera binata* contain numerous crystalline needles which closely resemble, but are not identical with, the crystalline tannin found by Molisch in *Dionœa muscipula* (A., 1916, i, 195). The latter is now found to contain both these compounds.
T. H. P.

The Proteoclastic Enzymes of Drosera rotundifolia. K. G. DERNBY (*Biochem. Zeitsch.*, 1916, **78**, 197—199).—The preparation used was a dialysed glycerol extract of the leaves. This contains a pepsin-like enzyme, but no trypsin or erepsin.
S. B. S.

Microchemistry of Plants. II. Orange-coloured Hydathodes in Ficus javanica. III. Brown Colouring Matter of "Golden-yellow" Grapes. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, **34**, 66—72).—Orange-yellow points occurring on the upper side of leaves of *Ficus javanica* are found to be due to numerous rounded or irregular bodies containing carotin.

The pale or dark brown ("goldgelbe") colour of that side of ripe green grapes which is exposed to the light is found to be due to the conversion of tannin into phlobaphen as a result of prolonged illumination. T. H. P.

Microchemistry of Plants. VIII. Readily Crystallisable Organic Substance in Linaria Species. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1917, **35**, 99—104).—The epidermis of *Linaria genistifolia* and of certain other species (*L. bipartita* and *L. reticulata*) contains an almost saturated solution of an organic substance which, shortly after the epidermis is placed in a drop of water on a microscope slide, crystallises out in single or twinned spherites, double brush forms, or prisms of a pale yellow colour. Treatment of the epidermis with alcohol, glycerol, acetone, ether, chloroform, sugar solution, xylene, 10% hydrochloric, nitric, or sulphuric acid, 5% oxalic acid solution, or concentrated acetic acid causes immediate precipitation of the substance. Sodium carbonate solution (10% or saturated) or 10% potassium carbonate solution colours the crystals an intense yellow, but does not dissolve them, whilst potassium, sodium, or barium hydroxide solution or ammonia solution dissolves them, giving yellow solutions. The substance occurs in the epidermis of all parts of the plant with the exception of the root. T. H. P.

Occurrence of ψ-Cubebin in Ocotea usambarensis, Engl. JOSEF HALBERKANN (*Arch. Pharm.*, 1916, **254**, 246—255).—The author has isolated from the bark of *Ocotea usambarensis*, Engl. (Ibean camphor tree), a substance, $C_{20}H_{20}O_6$, needles, m. p. 121·5—122°, $[\alpha]_D^{22}$ +60—61° in chloroform, which appears to be identical with Peinemann's ψ-cubebin. C. S.

Microchemistry of Plants. VII. Serratulin. HANS MOLISCH (*Ber. Deut. bot. Ges,*. 1916, **34**, 554—559).—The statement occurring in the literature to the effect that *Serratula tinctoria* contains in vivo a yellow colouring matter is erroneous. The cells of the living plant contain a colourless or almost colourless substance, serratulan, which undergoes post-mortem transformation, under the influence of various materials, into an intensely yellow substance, serratulin. Serratulan occurs in the root and stem, and in particular abundance in the leaves. T. H. P.

Action of Illuminating Gas on Plants. I. Action of the Gas on the Germination of Spores and Seeds. C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, **35**, 135—154).—The results of experiments made show that illuminating gas exhibits no general poisonous character towards plants. Anaerobic fungi grow even in the undiluted gas, and cress seeds (*Lepidium sativum*) remain alive in it for weeks. It retards the growth of the embryo, but this proceeds uninterruptedly if the gas is diluted with about five times its volume of air. Gas is thus not an acute plant poison, but if it is passed for some time through soil, the latter becomes incapable of permitting seeds to germinate and grow in it; after such soil has been extracted with cold water, it behaves normally towards seeds, the injurious properties being transferred to the water. The principal constituents of coal-gas to which its action on plants is due are sulphur compounds, benzene and its homologues, and, to a less extent, ethylene. Carbon monoxide is without effect on plants. T. H. P.

Physical Chemistry of Foods. III. The Chemical Equilibrium between Tartaric Acid and Potassium Tartrate as Basis of the Reduction of the Acidity of Wine by means of this Salt. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1917, **23**, 65—87. Compare A., 1915, ii, 590; this vol., i, 246).—Since the degree of acidity of a wine is identical with its hydrogen ion concentration, and the strength of the acid taste is directly proportional to this, it follows that the deacidification of wine by means of normal potassium tartrate brings about a reduction of the hydrogen ion concentration. The chemical equilibrium between tartaric acid and its potassium salt therefore plays an important part in the deacidification of wine by means of this salt. This equilibrium has been studied in the present paper, and the equations which express the equilibrium have been experimentally substantiated. A litre of pure, carbon dioxide-free water at 18° dissolves 4·903 grams = 0·02606 gram-mol. of potass-

ium hydrogen tartrate; the solubility product of this salt, $[K^{\cdot}]\cdot[HC_4H_4O_6{}']$, in water at 18° is equal to $3{\cdot}8 \times 10^{-4}$, in aqueous alcohol (8% alcohol) $1{\cdot}3 \times 10^{-4}$. The addition of ethyl alcohol, amounting to 80 grams per litre, therefore exerts a marked influence on the chemical equilibrium; further, the ionisation constant of tartaric acid in such a mixture is considerably less than in pure water. During the gradual deacidification of an aqueous solution of tartaric acid by means of normal potassium tartrate, the decrease in the acidity is much greater at the commencement than later. The titratable acid remains constant until the precipitation of potassium hydrogen tartrate commences, and then decreases in proportion to the amount of normal potassium tartrate added and the amount of potassium hydrogen tartrate precipitated. The values of the individual concentrations, both of ions and molecules during the deacidification of 10°/₀₀ aqueous or aqueous alcohol solutions of tartaric acid can be calculated by means of the equation put forward, and also the electrical conductivity of the equilibrium solutions can be calculated by the same means, giving values which agree well with the experimentally determined figures. When the deacidification process is carried out with natural wine, the same phenomena are, in general, observed as in the case of aqueous and aqueous-alcoholic solutions of tartaric acid. At the commencement, however, the decrease in the acidity is not so marked as with these solutions. This is due, in the first place, to the earlier precipitation of potassium hydrogen tartrate, since the wine usually contains a considerable amount of this salt. Further, the wine also contains considerable quantities of still weaker acids than tartaric acid. The deacidification of wine in this manner does not follow the simple equation $K_2C_4H_4O_6 + H_2C_2H_4O_6 = 2HKC_4H_4O_6$, as was previously believed, but is a much more complicated process. The following advantages are claimed for this method of deacidifying wine: (1) It introduces no foreign substance into the wine, since both potassium and tartaric acid are already there. (2) The greater part of the added substance is precipitated as potassium hydrogen tartrate, so that the ash and extract of the wine are not greatly increased. (3) This treatment does not so seriously change the constitution of the wine as does the deacidification with chalk. (4) Since normal potassium tartrate can be added to wine as a concentrated aqueous solution, which is impossible when chalk is used, the process is a homogeneous one from the beginning, and equilibrium is set up much more rapidly. Consequently, it is not necessary to keep the wine for long periods after deacidification; in general, it is found that the precipitation of potassium hydrogen tartrate is complete in twenty-four hours. This treatment does not produce a turbidity in the wine. (5) Since the degree of acidity of the wine remains the same, whether the solution is supersaturated with potassium hydrogen tartrate or not, the deacidification can be effected by simply running a solution of normal potassium tartrate into it until a sample possesses the correct taste.

J. F. S.

Physical Chemistry of Foods. IV. Scientific Wine Tests to Determine the Relationship between the Strength of the Acid Taste and the Hydrogen Ion Concentration. THEODOR PAUL (*Zeitsch. Elektrochem.*, 1917, **23**, 87—93. See preceding abstract).—An account of a number of experiments undertaken to show that it is possible to differentiate between and place in order a series of wines of different acidities. Moselle wine containing hydrogen ion of the concentrations 1·8, 0·95, 0·55, and 0·25 mg. ion per litre was submitted to sixty-four people. Of these, thirty-seven by taste alone correctly placed the four samples, eighteen people misplaced one sample, and to one person they all tasted alike. J. F. S.

An Artificial Soil, almost free from all Mineral or Organic Matter, suitable for the Study of Plant Cultures and for the Examination of the Influence of Different Fertilisers. A. GAUTIER (*Compt. rend.*, 1917, **164**, 985—986).—The medium is prepared by heating finely powdered coal to a red heat, boiling the product with acid, and finally washing it with distilled water. W. G.

Action of Various Salt Solutions on the Permeability of the Soil. D. J. HISSINK (*Bied. Zentr.*, 1917, **46**, 138—140).—Experiments with water and solutions of sodium, potassium, ammonium, and calcium chlorides indicate that the action of salt solutions on the permeability of the soil is not solely physical in character, but is probably dependent principally on chemical processes. T. H. P.

Relation of the Water-retaining Capacity of a Soil to its Hygroscopic Coefficient. FREDERICK J. ALWAY and GUY R. McDOLE (*J. Agric. Research*, 1917, **9**, 27—71).—A description of various experiments with uniform columns of soil of known hygroscopic coefficient and moisture equivalent to determine the distribution of water in the soil under different conditions. The soils used varied in texture from a coarse sand to a silt loam, having hygroscopic coefficients of 0·6 and 13·3 respectively.

Five such loams, placed in capillary connexion with a subsoil, were saturated with water from the top and allowed to remain protected from surface evaporation for several months. They lost water until the amount retained was from 2·1 to 3·1 times the hygroscopic coefficient of the particular soil. If a layer of coarse sand or gravel was interposed between the column of loam and the subsoil, the downward movement of the water in the loam was materially checked. Using a column made up of successive 5 cm. layers of loams differing in texture, the final water-content was independent of the order of their arrangement.

Using soil columns 75 to 85 cm. long, protected from all loss of moisture from the sides and bottom, but freely exposed to evaporation for times varying from three weeks to half a year, the moisture-content, originally uniform, fell until it reached, at depths below 30 cm., an almost constant minimum of 1·9 to 2·2 times the hygroscopic coefficient.

A comparison was made of twelve different loams, using 60 cm. columns and applying water in one series at the base and in the other at the top, in quantity sufficient to bring the average moisture-content of the columns up to 1·5 times their hygroscopic coefficient. The columns were protected at all surfaces from evaporation, and after four months the distribution of moisture with reference to the surface of application was found to be the same in each series. The maximum final ratio of moisture-content to hygroscopic coefficient was found in all cases in the 7·5 cm. adjacent to the surface of application, where it lay between 1·7 and 2·4. This ratio is not the same for all soils having the same hygroscopic coefficient. From these laboratory experiments the water-retaining capacity of the loams appears to bear a closer relationship to the moisture equivalent than to the hygroscopic coefficient.

Coarse sands behave very differently from loams. Three months after the application of 2·5 cm. of water, the surface 15 cm. section had a ratio of 6·0—7·0, whilst in the second 30 cm. it was only 1·0. These results were confirmed by field studies. Fine sands apparently occupy an intermediate position between the coarse sands and the loams.

Field studies show that loams, if thoroughly moistened with rain and protected from losses by evaporation and transpiration, lose water by downward movement until the ratio of moisture-content to hygroscopic coefficient lies between 1·8 and 2·5, and this is the ratio which may be expected in the subsoil, below the range of plant roots, in dry-land regions.

In cases where the subsoil has been previously exhausted of available water to a considerable depth by plants, it is found, even several months after heavy rain, that there is an abrupt transition from the moistened soil to the exhausted subsoil, the ratio dropping from 2·2 to 1·0. The moisture of the deeper subsoil will be able to move upward only so slowly and through such a short distance in a year as to be of no practical benefit to annual crops. In order to make use of it, deep-rooting perennials must be grown at intervals.

W. G.

Measurement of the Inactive, or Unfree, Moisture in the Soil by means of the Dilatometer Method. GEORGE J. BOUYOUCOS (*J. Agric. Research*, 1917, **8**, 195—217).—A dilatometer is described in which determinations have been made of the amount of water in soils failing to freeze when super-cooled to -3°. Various types of soil were examined, varying from a quartz sand to a heavy, black clay, and in each case the sample was prepared by adding 5 c.c. of water to 25 grams of air-dry soil. The bulb of the dilatometer was kept in a freezing mixture at -4°, and when the temperature inside the bulb was -3° the dilatometer was gently shaken until solidification began, and the expansion was read when equilibrium was reached. Under these conditions it was found that the amount of water failing to freeze varied from 2% in quartz sand to 80% in clay, of the water added. The more colloidal the character of the soil, the lower was the amount of water which

froze. The values obtained by this method correspond closely with the moisture contents known as the wilting coefficient, with the percentage of moisture at which solidification cannot be started and with the thermal critical moisture coefficient. This water which fails to freeze is designated as unfree or inactive water, and the evidence indicates that a large portion of it may exist as physically adsorbed and loosely chemically combined, the quantity of the latter probably exceeding that of the former. This inactive water is not in a stable condition, since the amount can be caused to vary by different modes of treatment. Thus in colloidal soils, increasing the super-cooling causes it to diminish, and a similar effect is obtained by increasing the degree of moisture content of the soil. Successive freezings also diminish the amount of water failing to freeze in colloidal soils. W. G.

Fixation of Ammonia in Soils. I. G. McBeth (*J. Agric. Research*, 1917, **9**, 141—155).—Many semi-arid subsoils have the property of fixing relatively large quantities of ammonia, a large percentage of the ammonia added in the form of ammonium salts not being recovered by the ordinary methods for determining the ammonia-content of soils. This fixation is not influenced by the anion of the ammonium salt. The ammonia added cannot be recovered by boiling the soil with excessive amounts of potassium or sodium hydroxide. Boiling with 10% hydrochloric acid in one case removed practically all the ammoniacal nitrogen and in another case 75% of it. The fixation of ammonia by semi-arid soils increases with the depth in the soil, with the concentration of the solution of the ammonium salt, and with rise in temperature. With the addition of small amounts of ammonium salts, the percentage fixation remains constant, but if increasing amounts are added the percentage fixation diminishes, whilst the absolute fixation tends to rise to a maximum. The fixation is most rapid during the first few minutes, and then proceeds slowly for several days. Heating the soil at 200° or above for six hours considerably reduces its power of fixing ammonia.

Aluminium, iron, and potassium salts added to soils prior to the addition of ammonia decidedly reduce the ammonia-fixing power of the soils, whilst calcium, magnesium, and sodium salts have but little effect on the ammonia-fixing power of these soils. The anions of these metallic salts do not exert any influence on these phenomena. In semi-arid soils the quantity of calcium brought into solution by ammonium chloride increases with the depth. When extracted with aluminium, sodium, or magnesium chloride, the calcium brought into solution does not increase with the depth.

W. G.

Availability of Potash in certain Orthoclase-bearing Soils affected by Lime or Gypsum. Lyman J. Briggs and J. F. Breazeale (*J. Agric. Research*, 1917, **8**, 21—28).—Experiments with pegmatite and orthoclase show that the solubility of their potassium in water is not affected by the presence of calcium hydr-

oxide. The presence of calcium sulphate tends to diminish the solubility of the potassium in the orthoclase, the solubility decreasing as the concentration of the calcium sulphate increases. Similar results were obtained with a virgin soil of granitic type, and these were confirmed by determining the potassium content of wheat seedlings grown on (*a*) water containing finely ground orthoclase, (*b*) the same saturated with calcium sulphate. W. G.

Transformation of the Sesquioxides in Woodland Soils. (Formation of Ortstein and Laterite.) H. STREMME (*Kolloid Zeitsch.*, 1917, **20**, 161—168).—The theory that ferric oxide and alumina in the soil are the result of the coagulation of corresponding sols, is examined in reference to the influence of the chemical and physical characters of the soil, climate, and vegetation. The composition of the soil solution, and in particular the amount of soluble organic substance present, is of primary importance in connexion with the coagulation process. H. M. D.

The Organic Matter of the Soil. V. The Nitrogen Distribution in different Soil Types. CLARENCE AUSTIN MORROW and ROSS AIKEN GORTNER (*Soil Sci.*, 1917, **3**, 297—331). —Three grams of fibrin were subjected to protein analysis by the Van Slyke method, the initial hydrolysis being carried out in presence of 100 grams of ignited subsoil. The figures thus obtained were compared with those of a similar analysis carried out without the presence of the soil, and it was found that the two sets of figures were in excellent agreement except for the fact that whereas the fibrin hydrolysed alone yielded 4·36% of its nitrogen in the histidine fraction and 2·83% as 'humin,' the fibrin hydrolysed with the subsoil yielded no histidine nitrogen and 7·59% of 'humin.' Although it appeared likely that the presence of soil had caused the histidine nitrogen to be converted into 'humin' nitrogen, pure histidine dihydrochloride underwent no such conversion when boiled with hydrochloric acid for forty-eight hours in presence of subsoil. The Van Slyke method of protein analysis was then applied to a series of soils of various types, and the authors point out that although the data obtained for the different fractions may not be comparable to similar data obtained from pure proteins, they are of value for comparing the distribution of the nitrogen amongst the different fractions in various soil types. The results of the analyses showed that when expressed as a percentage of the total nitrogen in the soil, the nitrogen dissolved by the acid hydrolysis was practically constant, irrespective of the nature or the condition of the soil under investigation. The same is true of all the other fractions isolated, and the conclusion may be drawn that the organic compounds of nitrogen in different soil types are very uniform.

As a result of their investigations, the authors suggest the advisability of estimating a further fraction in connexion with the 'humin' nitrogen. L. M. U

Organic Chemistry.

The System Water–Uranyl Oxalate–Sodium Oxalate. A. COLANI (*Compt. rend.*, 1917, **165**, 111—113).—An examination of the solubility curves of the system water–uranyl oxalate–sodium oxalate at 15° and 50° shows the existence of two new compounds having the composition $Na_2(UO_2)_4(C_2O_4)_5,11H_2O$ and $Na_2(UO_2)_2(C_2O_4)_3,5H_2O$. In addition, a pentahydrate,

$$Na_2(UO_2)(C_2O_4)_2,5H_2O,$$

was obtained, the crystals of which were macroscopically identical with those of the hexahydrate described by Wyrouboff (compare *Bull. Soc. franc. Min.*, 1909, **32**, 351, 357, 364). No indication of the salt $Na_6(UO_2)_2(C_2O_4)_5,13H_2O$ described by Wyrouboff (*loc. cit.*) could be obtained. At 75°, from a solution containing 1·5 mols. of sodium oxalate to 1 mol. of uranyl oxalate, crystals were deposited having the composition $Na_{10}(UO_2)_4(C_2O_4)_9,12H_2O$.

W. G.

Isomerisation and Hydration of Citronellaldehyde by Acids. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 627—630).—Formic acid (85—90%) or phosphoric acid (80%) converts citronellaldehyde into an oil which, on distillation in a vacuum, yields 10% of *iso*pulegol; 15—20% of a condensation product of 2 molecules of citronellaldehyde, b. p. 185°/13 mm.; *iso*pulegol hydrate, acicular crystals, m. p. 84—85°; and a heptacyclic glycol, $C_{10}H_{20}O_2$, m. p. 60—62°.

A. J. W.

Action of Acids on the Rotatory Power of Sucrose and Invert-sugar in the Presence of Soluble Salts. EM. SAILLARD (*Compt. rend.*, 1917, **165**, 116—118).—[With WEHRUNG.]—Sulphurous and acetic acids, at the concentrations used, have no effect on the rotatory power of sucrose in the presence of sodium chloride, but they diminish that of invert-sugar in the presence of this salt, to which they are thus antagonistic. Hydrochloric acid increases the lævorotatory power of invert-sugar in the presence of sodium chloride. Carbon dioxide is without action on the rotatory power of either sucrose or invert-sugar in the presence of sodium chloride.

W. G.

The Chemistry of Caramel. I. Caramelan. MARY CUNNINGHAM and CHARLES DORÉE (T., 1917, **111**, 589—608).—Believing that a study of the process of the formation of caramel may have a bearing on the problem of the constitution of cellulose and the question of the production of humus, peat, and coal, the authors have begun a systematic investigation by a contribution on the nature of caramelan.

When sucrose is heated at 170—180° until the loss of weight is

12%, it loses two molecules of water, some furfuraldehyde, pungent acid vapours, and carbon dioxide being evolved as well, and leaves practically pure caramelan, $C_{12}H_{18}O_9$, or probably $C_{24}H_{36}O_{18}$, m. p. 136°. This yields a tetra-acetate, m. p. 107°, a *tetrabenzoate*, m. p. 105—108°, and an explosive *tetranitrate*. It behaves like a ketose in forming precipitates with resorcinol and phloroglucinol, and it also condenses with phenylhydrazine and semicarbazide, but the products are not simple hydrazones or semicarbazones, but derivatives of a $C_{24}H_{36}O_{18}$ molecule less several molecules of water. When shaken with 40% hydrochloric acid, caramelan is not hydrolysed as is cellulose, or hydrolysed and then converted partly into ω-chloromethylfurfuraldehyde like sucrose, but is dehydrated further to caramelin, $C_{24}H_{26}O_{13}$. Dilute sulphuric and hydrochloric acids, however, cause hydrolysis and dehydration at the same time, dextrose, methylfurfuraldehyde, furfuraldehyde, humic acid, $C_{24}H_{22}O_{11}$, and a chlorinated humic acid, $C_{24}H_{29}O_{18}Cl_3$, having been found among the products.

The action of various oxidising agents on caramelan has also been investigated. The products are very complex, but are mostly derivatives of a C_{23} unit. Acetaldehyde was obtained from the ozonide, indicating that a CHMe:C residue is present in caramelan, whilst dilute nitric acid yielded an insoluble, red, nitrated humic acid, $C_{23}H_{23}O_{12}\cdot NO_2$, and a soluble, ketonic nitro-acid, $C_{11}H_{15}O_{10}N$.

J. C. W.

Constitution of the Salts of *S*-Alkylthiocarbamides. JOHN TAYLOR (T., 1917, **111**, 650—663).—Additive compounds of thiocarbamide with alkyl haloids have been known for a long time. Similar compounds with methyl, benzyl, and ethyl sulphates, nitrates, and thiocyanates have now been obtained, the readiness with which combination takes place falling off in the order in which the radicles are named, which is the same as in the case of the haloids. These compounds all behave like salts, in which the acidic ions respond to the usual tests. From one salt another can be made by double decomposition, so that it is possible to prepare salicylates, acetates, and phosphates, which cannot be obtained directly. Two formulæ only need therefore be considered in connexion with the constitution of these additive compounds, namely, the "sulphonium" (I) and "ammonium" (II):

$$\begin{matrix}NH_2 \\ NH_2\end{matrix}\!\!>C{:}S\!<\!\!\begin{matrix}R \\ X\end{matrix} \qquad\qquad \begin{matrix}NH \\ XNH_3\end{matrix}\!\!>C\cdot S\cdot R$$

(I.) (II.)

Since the compounds with benzyl nitrite and methyl and benzyl thiocyanates are stable in boiling water, the ammonium type is improbable, but in the case of benzyl esters of strong acids, two isomerides are met with, and one of them is then of this type. The conditions for the formation of the ammonium salts are that the free mineral acids shall be present during the crystallisation of the salt, and the sulphonium salts can be obtained from them

by boiling with water alone or with a very dilute aqueous or alcoholic solution of sodium phosphate. Salts prepared by double decomposition are always of the sulphonium type, even if an "ammonium" salt is used.

Nencki (1874) described an additive compound of thiocarbamide with ethyl oxalate which has m. p. 158°, does not give a precipitate of calcium oxalate until hydrolysed, and yields a metallic sulphide when warmed with alkaline lead solutions or ammoniacal silver nitrate. An isomeride of the sulphonium type,

$$C(NH_2)_2{:}SEt{\cdot}CO_2{\cdot}CO_2{\cdot}S{\cdot}CEt(NH_2)_2,$$

is obtained if the compound of thiocarbamide with ethyl iodide is treated with silver oxalate. This has m. p. 188°, gives a precipitate of calcium oxalate at once, and produces metallic mercaptides and cyanamides with the above lead or silver solutions.

When thiocarbamide oxalate is warmed with alcohol, Nencki's compound is formed. This is explained by assuming that oxalic acid is given up by the thiocarbamide salt, that ethyl oxalate is then formed, and that this ester combines with the free thiocarbamide. Such evidence was required when a similar explanation of the action of acetaldehyde on thiocarbamide hydrochloride was advanced (Dixon and Taylor, this vol., i, 11).

For the details of the numerous salts, many of which had been described by Arndt as salts of alkyl-ψ-thiocarbamides (A., 1911, i, 918), the original should be consulted. J. C. W.

Diazomethane. F. H. Loring (*Chem. News*, 1917, **115**, 255).—An ethereal solution of diazomethane is obtained by distilling from a retort in a water-bath a mixture of 2·5 c.c. of nitrosomethylurethane, 25 c.c. of dry ether, and 1·75 c.c. of methyl-alcoholic potassium hydroxide (1 : 4), and collecting the distillate in a freezing mixture of ice and calcium chloride. G. F. M.

Preparation of Benzenesulphonic Acid. Comp. des Produits Chimiques d'Alais and de la Camargue (Brit. Pat., 101973, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 705).—Benzenesulphonic acid is prepared by passing benzene vapour into sulphuric acid of any concentration, preferably at 120—130°. Water is eliminated as steam, and the sulphonic acid crystallises on cooling. D. F. T.

Method of Separating Benzenedisulphonic Acid from Sulphuric Acid and Converting it into a Salt. L. M. Dennis (U.S. Pat., 1227252, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 705).—The mixture of disulphonic acid and sulphuric acid is extracted with an organic solvent, for example, benzene, and the resulting solution is treated with a suitable compound to convert the dissolved disulphonic acid into a salt. D. F. T.

The Alcohols and Bases of Vacuum Tar. Amé Pictet, O. Kaiser, and A. Labouchère (*Compt. rend.*, 1917, **165**, 113—116).—The authors have isolated from vacuum tar 4-methyl*cyclo*hexanol, and the alcohols from C_8 to C_{11}, inclusive, of the

homologous series $C_nH_{2n-6}O$. The last four alcohols are unsaturated, and are spontaneously and fairly rapidly converted into phenols, this process being accelerated by heat. Their acetates, which are colourless, volatile liquids, instantly decolorise potassium permanganate in cold sulphuric acid solution. The bases isolated consist of a product, C_7H_9N, and the members from C_8 to C_{12}, inclusive, of the homologous series $C_nH_{2n-9}N$. The first-named base is probably a mixture of toluidines. The other bases are unsaturated, secondary amines, with odours resembling those of quinoline and its homologues. The physical properties of the alcohols and their acetates, and the bases and their picrates, are as follows:

Alcohols.			Bases.		
		Acetate.			Picrate.
Formula	B. p.	B. p.	Formula.	B. p.	M. p.
$C_7H_{14}O$ ...	170—175°		C_7H_9N	198—203°	170°
$C_8H_{10}O$ ...	185—190		C_8H_7N	225	195
$C_9H_{12}O$ ...	198—200	213—215°	C_9H_9N	247—250	184
$C_{10}H_{14}O$ ...	213—215	226—229	$C_{10}H_{11}N$	250—260	184
$C_{11}H_{16}O$ ...	226—228	240—244	$C_{11}H_{13}N$	260—265	173
			$C_{12}H_{15}N$	270—280	166

W. G.

Sozoiodol-Mercury Compounds. E. Rupp and A. Herrmann (*Arch. Pharm.*, 1916, **254**, 488—497).—Pharmaceutical preparations containing organic mercury compounds belong to two classes, namely, those containing ionisable mercury, for example, hydrargyrum benzoicum, and those, such as hydrargyrum salicylicum, containing nuclear, non-ionisable mercury. Some such preparations, which are insoluble in water, dissolve readily in a solution of sodium chloride. This solubility is due, in the case of substances of the former class, to ordinary double decomposition with formation of mercuric chloride, and in the case of substances of the latter class to the formation of the sodium salts of chloromercuri-aromatic acids by the addition of sodium chloride.

Sozoiodol-mercury $\left(C_6H_2I_2<\begin{smallmatrix}O-\\SO_3\end{smallmatrix}>Hg\right)$ belongs to neither of the preceding classes, and therefore the cause of its solubility in a solution of sodium chloride or potassium iodide has been investigated, and also the explanation of its orange colour. The substance has been prepared in several different ways: (1) by the reaction in hot aqueous solution between mercuric nitrate and an equivalent amount or an excess of sodium sozoiodolate (2:6-diiodophenol-*p*-sulphonate); (2) from yellow mercuric oxide and an equivalent quantity or an excess of sozoiodolic acid in aqueous solution; and (3) by adding a warm aqueous solution of sodium sozoiodolate to the equivalent amount of a mercuric acetate solution. If in the last method the order of the addition is reversed and the solutions are at the ordinary temperature, a red *substance*, $(SO_3Na{\cdot}C_6H_2I_2{\cdot}O)_2Hg$, is at first precipitated, which is converted into sozoiodol-mercury by the addition of more mercuric acetate

solution. This red substance is better obtained by digesting yellow mercuric oxide and sodium sozoiodolate (2 mols.) in lukewarm water; it dissolves in aqueous sodium chloride, forming a colourless solution.

When a solution of sozoiodol-mercury in aqueous sodium chloride is extracted with ether, the extract is found to contain mercuric chloride in nearly the theoretical amount corresponding with the equation

$$C_6H_2I_2{<}{}^{O-}_{SO_3}{>}Hg + 2NaCl = HgCl_2 + ONa{\cdot}C_6H_2I_2{\cdot}SO_3Na.$$

The disodium sozoiodolate is difficult to isolate on account of its great solubility, but when a concentrated solution of sozoiodol-mercury in aqueous sodium chloride is acidified, sodium sozoiodolate is precipitated in slender needles containing $2H_2O$. The disodium salt forms large, rectangular crystals containing $5H_2O$, having a faintly alkaline reaction. The dipotassium salt is formed, together with potassium mercuric iodide, when sozoiodol-mercury dissolves in aqueous potassium iodide; by adding the latter very carefully, mercuric iodide is obtained in quantitative amount.

The brick-red *substance*, $C_6H_2I_2{<}{}^{O-Hg-O}_{SO_3{\cdot}Zn{\cdot}SO_3}{>}C_6H_2I_2$, is obtained by digesting mercuric oxide and zinc sozoiodolate with warm water; it resembles the corresponding sodium salt in its behaviour. These two substances are coloured, and so also is *mercuric* 2:4:6-*tribromophenoxide*, $(C_6H_2Br_3{\cdot}O)_2Hg$, yellowish-red crystals, prepared from mercuric acetate and tribromophenol in aqueous-alcoholic solution; it appears, therefore, that the group ·O·Hg·O· exerts a chromophoric function, and thus the colour of sozoiodol-mercury is accounted for.

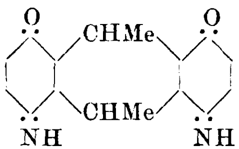
Potassium 2:6-*di-iodophenetole*-p-*sulphonate*, $OEt{\cdot}C_6H_2I_2{\cdot}SO_3K$, colourless needles, is prepared by heating potassium sozoiodolate (1 mol.) and potassium hydroxide (1·1 mols.) dissolved in a little water with an alcoholic solution of ethyl iodide (1·1 mols.) at about 130°. The corresponding *barium* salt, needles with $5H_2O$, and *mercuric* salt, colourless needles, have been prepared; 2:6-*di-iodophenetole*-p-*sulphonic acid* forms crystals with $2H_2O$, m. p. 108°.

The constitution of sozoiodolic (2:6-di-iodophenol-*p*-sulphonic) acid is proved by the facts that the acid (1) yields 2:4:6-tri-iodophenol, iodine, and phenol by heating with fuming hydrochloric acid at about 120°, and (2) is formed by treating 2:6-dihydroxymercuriphenol-*p*-sulphonic acid (Rupp and Herrmann, this vol., i, 488) with a solution of iodine.

Anogon ($OHg{\cdot}C_6H_2I_2{\cdot}SO_3Hg$) does not form a clear solution in aqueous sodium chloride, a precipitate of mercurous chloride being produced. C. S.

Action of Acetaldehyde-ammonia on Quinones. PRAPHULLA CHANDRA GHOSH (T., 1917, **111**, 608—612).—*p*-Benzoquinone condenses with acetaldehyde-ammonia to form a black

compound, probably of the annexed formula, which reacts with cold nitric acid (D 1·45) to form a yellow *compound*, $C_{16}H_{12}O_6N_4$. These do not melt at 290°. Anthraquinone and acetaldehyde-ammonia react at 220° to yield a colourless, silky *compound*, m. p. 281°, to which the formula $C_6H_4<\begin{matrix}C(:CH\cdot CHO)\\C(:CH\cdot CHO)\end{matrix}>C_6H_4$ is assigned, since it forms a yellow *phenylhydrazone*, $C_{18}H_{12}(:N\cdot NHPh)_2$. J. C. W.



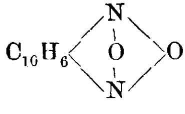
A Simple Demonstration of the Addition of Water to Terpineol under the Influence of Acids. H. J. Prins (*Chem. Weekblad*, 1917, **14**, 630—631).—When terpineol is agitated with 80% phosphoric acid at 30°, it dissolves, and crystals of terpin hydrate separate. A less complete transformation is caused by 60% sulphuric acid, but 85% formic acid does not react.

A. J. W.

The Bromo-derivatives of Aloe-emodin. E. Léger (*J. Pharm. Chim.*, 1917, [vii], **16**, 5—8).—When aloe-emodin is heated in a sealed tube at 115° for eighteen hours with bromine, *pentabromoaloe-emodin*, $C_{15}H_5O_5Br_5$, slender, prismatic needles, m. p. 278·4° (corr.), is obtained. This compound is only very slowly soluble in cold dilute alkali hydroxide, but it dissolves at once on warming, and is converted into *tetrabromoaloe-emodin*, orange-red needles, m. p. 276·4° (corr.). W. G.

Equilibrium in the System: Cupric Chloride-Pyridine. J. Howard Matthews and Samuel Spero (*J. Physical Chem.*, 1917, **21**, 402—406).—Measurements of the solubility of cupric chloride in pyridine at temperatures between −17° and 95° show the existence of three compounds: $CuCl_2,6C_5H_5N$, which is the stable solid phase up to −10°; $CuCl_2,2C_5H_5N$, stable between −10° and 58°; and $2CuCl_2,3C_5H_5N$, which is the stable phase above 58°. The first of the three compounds has not been previously described. H. M. D.

Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides, and of *o*-Nitrosoamines into *iso*Oxadiazoles. Arthur G. Green and Frederick Maurice Rowe (T., 1917, **111**, 612—620).—In three earlier papers (T., 1912, **101**, 2452; 1913, **103**, 897, 2023), it was shown that many *o*-nitroamines are converted into *iso*oxadiazole oxides (furoxans, furazan oxides) when oxidised by alkaline sodium hypochlorite. 2-Nitro-1-naphthylamine and 1-nitro-2-naphthylamine are no exceptions to this generalisation, for they both yield the same naphth*iso*oxadiazole oxide or naphthafuroxan (annexed formula), m. p. 127°. This compound is the "β-naphthaquinonedioxime peroxide" of Forster and Fierz (T., 1907, **91**, 1942) and also the "1:2-dinitrosonaphthalene" of Koreff and Ilinski. It yields β-naphthaquinonedioxime on reduction with



hydroxylamine, and this gives *naphthisooxadiazole* (*naphthafurazan*), $C_{10}H_6<\overset{N}{\underset{N}{|}}>O$, m. p. 78°, on boiling with sodium hydroxide.

8-Nitro-1-naphthylamine does not yield a furoxan by this treatment, and 2:4-dinitronaphthylamine suffers rupture of the ring, which agrees with the authors' earlier experiences and interpretation of the mechanism of the reaction.

The oxidation of *o*-nitrosoamines by sodium hypochlorite is a similar reaction; the base passes through a quinonoid state to an *iso*oxadiazole (furazan). Thus, 1-nitroso-2-naphthylamine and 2-nitroso-1-naphthylamine both yield the above naphth*iso*oxadiazole. Similarly, *o*-nitrosoacetanilide (the free base could not be prepared) suffers hydrolysis and oxidation simultaneously, and gives benz*iso*oxadiazole (benzfurazan). Crude *m*-nitrosoaceto-*p*-toluidide likewise gives 5-methylbenz*iso*oxadiazole, $C_6H_3Me<\overset{N}{\underset{N}{|}}>O$ (compare T., 1913, **103**, 2023). J. C. W.

The Mechanism of the Ninhydrin Reaction. A Contribution to the Theory of Colour of Salts of Alloxantin-like Compounds. J. M. RETINGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1059—1066. Compare Ruhemann, T., 1911, **99**, 792, 1306). —A theoretical discussion of work published elsewhere (Diss., Leipzig, 1913) in which the author suggests the following course for the whole ninhydrin reaction. The triketohydrindene hydrate hydrolyses during boiling, giving *o*-carboxyglyoxal, which reduces part of the triketohydrindene to dioxindone, which then combines with another molecule of triketohydrindene to give hydrindantine. The amino-acid or amine derived from the enzyme action gives, first, as has been shown in the alloxantin series on alkali salts (*loc. cit.*), a monobasic salt which is colourless; further boiling produces a dibasic neutralisation, and the molecule then splits into two molecules with tervalent carbon, having a free valency, this being the cause of the absorption in the visible spectrum. The difference in colour at this stage is due to the different sizes of the molecules connected with the tervalent carbon, which results in a different potential for the free affinity of the carbon, and thus a different optical effect. Exposure to air in aqueous solution decomposes the split molecules further, giving *o*-carboxymandelic acid, ammonia, carbon dioxide, water, and an aldehyde. W. G.

Acid Hæmochromogen. CH. DHÉRÉ (*Compt. rend. Soc. de Biol.*, 1917, **79**, 1087—1090; from *Physiol. Abstr.*, 1917, **2**, 224). —A description of simple methods for preparing acid hæmochromogen by means of sodium hyposulphite. Acid hæmochromogen is more soluble in acetone than in methyl or ethyl alcohol. It is also soluble in ether, in methylal, in amyl alcohol, in benzene, and in toluene. It is not soluble in light petroleum,

and apparently not in glycerol. The solutions are stable for some months. G. B.

The "Mechanical Denaturation" of Proteins and the Method of Drying Organs for Biological Investigation. WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1917, **81**, 278—283).—The author confirms the observations of Herzfeld and Klinger (this vol., i, 300), according to which proteins dried on a plate become insoluble on scraping. For this reason, when organs are dried, the manipulation must be carried out in such a way that they can be dried into powder form and readily removed without such mechanical action from the material upon which they are spread. For this purpose, plates coated with solid paraffin can be used, and a preliminary account is given of a drying oven which can be employed, and which is designed to prevent the powder of the dried organs from being scattered by the current of air. S. B. S.

Physiological Chemistry.

The Differential Blood-gas Apparatus of Barcroft. E. MÜNZER and W. NEUMANN (*Biochem. Zeitsch.*, 1917, **81**, 319—331).—An addition to Barcroft's apparatus is figured and described which has for its object its standardisation. This consists of a 1 c.c. pipette graduated in hundredths of a c.c., from which by means of a levelling tube a known volume of air can be driven into the manometer. The differences of level in the manometer corresponding with known volumes of air can thus be recorded when the standardisation is carried out at different atmospheric pressures and with different volumes in the pear-shaped vessels of the Barcroft apparatus. The constant k of the apparatus is obtained from the formula $v=kh$, where v is the volume of air driven in and h the difference in the heights of the olive oil in the two limbs of the manometer, and these are plotted for varying barometric heights and volumes of the pear-vessel. (In each case they are linear functions of these factors.) Attention is directed to an error in Barcroft's calculations, but it is pointed out that this does not materially affect his results. S. B. S.

The Presence of Phosphates in Human Blood-serum. I. The Phosphates Soluble in Acid in Normal and Pathological Sera. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **81**, 380—421).—A general discussion of the question of the amount of phosphate in serum, with a criticism of the analytical methods and a summary of results obtained, supplemented by a large number of analyses by the author. In normal cases, the amount of "soluble"

phosphorus is less than 4 mg. per 100 c.c. (90% of the cases), but it is occasionally higher, and has been found to reach the amount of 10 mg. per 100 c.c. In certain pathological cases the amount is much higher. S. B. S.

Acidosis. I. Concentration of Hydrogen Carbonate in the Blood Plasma; its Significance, and its Estimation as a Measure of Acidosis. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 289—346).—The work recorded in this and subsequent papers is based on the following hypothesis. Free carbon dioxide is present in the fluids of the body in such concentration that it automatically converts into hydrogen carbonate all bases not bound by other acids. The hydrogen carbonate, therefore, represents the excess of base which is left after all the non-volatile acids have been neutralised, and is available for the immediate neutralisation of further acids. In this sense it constitutes the "alkaline reserve" of the body. The concentration of hydrogen carbonate in the blood is representative of that in the body fluids in general, and is normally maintained at a constant level. Entrance of free acids reduces it to an extent proportional to the amount of the invading acid. Acidosis, therefore, is defined as a condition in which the concentration of hydrogen carbonate in the blood is reduced below the normal level.

The authors describe a method for estimating the concentration of hydrogen carbonate in the blood plasma under standard conditions. The plasma, from oxalated blood, drawn and centrifugalised under definite conditions, is shaken at the ordinary temperature in a separating funnel filled with alveolar air from the lungs of the operator or with an artificial air mixture containing 5·5% of carbon dioxide. The carbon dioxide in the plasma is then estimated by the method subsequently described (this vol., ii, 422). The results are calculated in terms of hydrogen carbonate by the aid of a table included in the text.

The average amount of carbon dioxide present as hydrogen carbonate in the plasma of normal men, estimated under the standard conditions, is 65 c.c. per 100 c.c. of plasma, the extreme limits being 77 and 53 respectively. In acidosis, the value obtained falls below normal, and is less the greater the severity of the prevailing acidosis condition. The method therefore constitutes a most sensitive indicator of this condition and can readily be applied clinically.

Experiments are also described showing the influence on the hydrogen carbonate of the plasma of various factors, in particular of the shift of bases and acids between plasma and corpuscles, under the influence of changing concentration of carbon dioxide in the blood. H. W. B.

Acidosis. III. Electrometric Titration of Plasma as a Measure of its Alkaline Reserve. GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 369—388. Compare van Slyke and Cullen, preceding abstract).—The method described is based on the hypothesis

that when a given amount of acid is added to a given volume of blood or plasma, the resultant change in the hydrogen-ion concentration (C_H) will be greater the less the alkaline reserve, or conversely, that when the alkaline reserve is low, less acid is necessary to produce a given increase in C_H. The amount of carbon dioxide in the plasma is first brought to a constant level by shaking with a known volume of air. It is then treated with an equal volume of $N/50$-hydrochloric acid, and the concentration of hydrogen ion estimated by the gas chain method. In an alternative procedure, the influence of carbon dioxide is removed by adding 2 volumes of $N/50$-hydrochloric acid to the plasma and exhausting the solution before estimating the hydrogen-ion concentration. The results obtained from the two procedures are different, but run parallel under varying conditions (compare Stillman and collaborators, this vol., i, 523) with the capacity of the plasma for combining with carbon dioxide. The electrometric titration constitutes, therefore, a trustworthy index of the alkaline reserve actually existing in the body. H. W. B.

Acidosis. IV. Relationship between Alkaline Reserve and Acid Excretion. REGINALD FITZ and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **30**, 389—400. Compare preceding abstract).—The introduction of an acid into the circulatory system immediately reduces the amount of alkali hydrogen carbonate in the blood, and is followed by an increased rate of excretion of ammonium salts, acid phosphates, and other acid substances in the urine. The authors find that this relationship is quantitative and can be expressed empirically by a formula similar to that devised by Ambard to denote the relationship between blood concentration and excretion in the cases of salt and urea. If D represents the rate of excretion of ammonia plus titratable acid, expressed as the equivalent number of c.c. of $N/10$-acid passed in twenty-four hours, C the concentration of ammonia plus titratable acid in the urine, also expressed in c.c. of $N/10$-acid per litre, and W the body-weight in kilograms, then the volume of carbon dioxide in 100 c.c. of the blood plasma, estimated by van Slyke's method, is $80 - \sqrt{(D/W \, . \, \sqrt{C})}$. The data can be estimated by analysis of the urine passed in twenty-four hours or from the amount excreted in one or two hours, multiplied to bring it to the twenty-four-hour basis. The results are accurate within 10 volumes per cent. The calculation is simplified by the use of a series of curves given in the text, by means of which the index can be read off at once when the volume of urine passed per kilogram of body-weight per twenty-four hours and the amount of ammonia plus titratable acid per litre of the urine are known.

This relationship holds in the case of diabetics as well as of normal persons, but diabetics receiving carbonate administrations are exceptions, the carbon dioxide in the plasma being, as a rule, much higher than that calculated from the urinary analysis.

H. W. B.

Acidosis. V. Alveolar Carbon Dioxide and Plasma Hydrogen Carbonate in Normal Men during Digestive Rest and Activity. DONALD D. VAN SLYKE, EDGAR STILLMAN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1917, **30**, 401—404. Compare A., 1915, i, 733, and preceding abstracts).—In the normal person, the volume of carbon dioxide present as hydrogen carbonate in 100 c.c. of blood plasma varies between 53 and 78 c.c. The ratio of plasma hydrogen carbonate to alveolar carbon dioxide tension, measured in millimetres of mercury, varies from 1·27 to 1·80. The alveolar carbon dioxide tension rises after a meal, whilst the plasma hydrogen carbonate sometimes slightly increases and at other times remains unchanged. The change in alveolar carbon dioxide after a meal is therefore probably due to an action on the respiratory centre (Higgins, A., 1914, i, 613) and not to a change in the hydrion concentration of the blood due to the secretion of gastric juice (*loc. cit.*). H. W. B.

Acidosis. VI. Blood, Urine, and Alveolar Air in Diabetic Acidosis. EDGAR STILLMAN, DONALD D. VAN SLYKE, GLENN E. CULLEN, and REGINALD FITZ (*J. Biol. Chem.*, 1917, **30**, 405—456. Compare preceding abstracts).—The authors have measured the alveolar carbon dioxide tension, the carbon dioxide present as hydrogen carbonate in the blood and in the blood plasma, the hydrogen-ion concentration of the plasma, and the index of acid excretion in the urine in a number of diabetics. Curves are drawn indicating the variations in these factors from day to day, and it is noted that there is a general parallelism between all the curves. The agreement between the factors relating to the urine and blood is on the average more accurate than that of the alveolar air and blood, and is observed, not only in adults, but also in children of as little as 25 kilograms of body-weight. In very severe acidosis, however, the urine index is less accurate than the alveolar air in indicating the alkaline reserve.

The results indicate the existence of the following relations between the intensity of the acidosis and the volume of carbon dioxide in c.c. present as hydrogen carbonate in 100 c.c. of blood plasma: normal resting adult, 77—53; mild acidosis, 53—40; moderate acidosis, 40—30; severe acidosis with symptoms of acid intoxication, below 30. The lowest volume of carbon dioxide recorded in which recovery occurred is 16. H. W. B.

Non-protein Nitrogen of Blood: 1. Removal of the Protein. 2. Estimation of Creatine. ISIDOR GREENWALD (*Proc. Soc. exp. Biol. Med.*, 1917, **14**, 115—117. Compare A., 1916, ii, 62).—Blood is run into boiling 0·01*N*-acetic acid, and the last traces of protein are removed by thoroughly shaking the filtrate (from the coagulum) with kaolin. Kaolin also quantitatively adsorbs creatinine, but creatine not at all. By evaporating the filtrate from kaolin with acid (filtrate from 50 c.c. of blood with 10 c.c. of *N*-hydrochloric acid to a volume of 5—10 c.c.), a solution is obtained giving with picric acid a solvent reaction like that of crea-

tinine and corresponding with 4 mg. of creatine per 100 c.c. of blood. It is not certain whether the reaction is indeed due to creatinine, but added creatine is quantitatively accounted for. G. B.

Chemical Evidence of the Presence of Glycogen-like Polysaccharide in the Liver-blood of Diabetic Animals. J. J. R. Macleod (*Proc. Soc. exp. Biol. Med.*, 1917, **14**, 124—125).—In hyperglycæmic and diabetic dogs and rabbits the blood from the liver contains a polysaccharide, giving a reddish-violet colour with iodine and precipitated by alcohol and sodium chloride. On hydrolysis, a reducing sugar is formed. The amount is very small. G. B.

A Study of Methods of Estimation of Metabolic Nitrogen. E. B. Forbes, C. E. Mangels, and L. E. Morgan (*J. Agric. Research*, 1917, **9**, 405—411).—Five pigs were fed on a basal ration of corn, supplemented in succeeding periods with dried blood, skim milk, and egg-albumin. The metabolic nitrogen was determined in the fæces from these periods by three methods, namely: (1) the acid–pepsin method; (2) the acid–pepsin and alkaline–pancreatin method; (3) Jordan's method, consisting of successive extractions with ether, boiling alcohol, boiling water, and cold saturated calcium hydroxide solution. The apparent digestibility of the protein of the corn was 75%. Allowing for the metabolic nitrogen, the real digestibilities obtained were, by method (1) 92%, by method (2) 96%, and by method (3) 86%. All three methods make the nitrogen of blood albumin appear more than completely digestible, the feeding of blood albumin apparently increasing the digestibility of the corn protein. In comparing the three methods, it seems probable that methods (1) and (2) give results which are more nearly true than those from Jordan's method, which does not digest bacteria. W. G.

Nutrition Investigations on Cotton-seed Meal. II. Anna E. Richardson and Helen S. Green (*J. Biol. Chem.*, 1917, **30**, 243—258. Compare A., 1916, i, 581).—The results previously obtained (*loc. cit.*) are confirmed. Normal growth and reproduction are observed in the case of albino rats on a diet containing 50% of cotton-seed flour, provided sufficient butter fat and protein-free milk are also administered. Toxic effects are not observed even in feeding 50% of cotton-seed flour to rats through four successive generations, but small amounts of crystallised gossypol prepared from cotton-seed kernels cause rapid loss in weight and death of the animals. H. W. B.

Biological Efficiency of Potato Nitrogen. Mary S. Rose and Lenna F. Cooper (*J. Biol. Chem.*, 1917, **30**, 201—204).—Nitrogenous equilibrium can be maintained on a diet in which potato constitutes practically the sole source of protein. H. W. B.

Rôle of Yeast in the Nutrition of an Insect (Drosophila). J. H. NORTHROP (*J. Biol. Chem.*, 1917, **30**, 181—187. Compare Loeb and Northrop, this vol., i, 65).—Experiments are described the results of which indicate that yeast contains a sufficient excess of accessory substances to render available for the nutrition of the banana fly approximately twice as much food material as is contained in the yeast. For instance, the rate of growth of the larvæ is equally rapid on mixtures of banana and yeast containing 33% or more of yeast as it is on yeast alone. In mixtures containing less than this proportion of yeast, growth becomes slower as the percentage of yeast is decreased, and finally, when the proportion of yeast is very small, becomes abnormal. Casein and sugar may serve as adequate food material for growing larvæ provided a sufficient proportion of yeast is also present.

Various tissues have been employed as the sole source of nutritive material for the growing larvæ; the kidney, liver, and pancreas of the dog, liver from the mouse, and the bodies of the flies themselves are found to permit of normal growth, whilst the spleen, muscle, blood, adrenal and thyroid glands from the dog and the muscle and testis from the mouse are inadequate. The larvæ grow normally on any tissues when they are infected with bacteria. Certain tissues therefore contain the requisite accessory substances which are absent from others. H. W. B.

Synthesis of Peptides in the Animal Organism. HERMANN PAULY (*Zeitsch. physiol. Chem.*, 1917, **99**, 161—165).—The author suggests that in the animal organism the combination of amino-acids to form peptides, and eventually proteins, does not occur directly, but by a succession of reductions and oxidations. An amino-acid is readily reduced to an aldehyde, and if combination with another amino-acid should ensue, the resulting compound on oxidation should yield a peptide in accordance with the following equations: $X{\cdot}NH{\cdot}CH_2{\cdot}CO_2H + H_2 = X{\cdot}NH{\cdot}CH_2{\cdot}CHO + H_2O$,

$$X{\cdot}NH{\cdot}CH_2{\cdot}CHO + NH_2{\cdot}CH_2{\cdot}CO_2H = X{\cdot}NH{\cdot}CH_2{\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2H + H_2O,$$

$$X{\cdot}NH{\cdot}CH_2{\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2H + O = X{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H.$$

The last reaction involves the oxidation of the group $\cdot CH{:}N\cdot$ to $\cdot C(OH){:}N\cdot$, followed by tautomeric change to $\cdot CO{\cdot}NH\cdot$.

In support of his views, the author finds that when neutral aqueous solutions of benzaldehyde and glycine are mixed and oxidised at the ordinary temperature with potassium permanganate, a small proportion of hippuric acid is produced.

H. W. B.

The Cerebrosides of Brain Tissue. P. A. LEVENE and C. J. WEST (*Proc. Soc. exp. Biol. Med.*, 1917, **14**, 93—95).—The authors now accept the nomenclature of Thudichum. In confirmation of previous work (compare also Rosenheim, A., 1916, i, 493), it is held that the only point of difference in the

composition of the dextrorotatory phrenosin and the lævorotatory kerasin is in the nature of one component, namely, the fatty acid. Following a suggestion of Rosenheim, an unsuccessful attempt was made to separate phrenosin and kerasin by means of the different solubility of their benzoyl derivatives, but it is hoped that a repeated benzoylation of the lævorotatory fraction may finally lead to a successful separation of kerasin. By a new method of hydrolysis, the previous statements as to the percentage of galactose in the substances were confirmed. G. B.

Enzyme and Reaction of Medium in Autolysis. MAX MORSE (*J. Biol. Chem.*, 1917, **30**, 197—199).—In the autolysis of the liver of the guinea-pig, the proteolytic enzyme is active only when the medium is acid. H. W. B.

The Active Principle of the Pituitary Gland. M. GUGGENHEIM (*Biochem. Zeitsch.*, 1917, **81**, 274—277).—A reply to the criticism of the author's work by Fühner (A., 1916, i, 778). S. B. S.

Thermal Decomposition of the Active Principle of the Pituitary Gland. H. S. ADAMS (*J. Biol. Chem.*, 1917, **30**, 235—242).—The active principle contained in an extract of the pituitary gland is rapidly destroyed at 100° when the hydrogen-ion concentration of the solution is of the order of $N \times 10^{-5}$. The destruction proceeds in a manner characteristic of a single substance, decomposing according to the law for a unimolecular reaction, and is not accelerated by oxygenation. When the hydrogen-ion concentration is increased to $N \times 10^{-3}$, the active principle becomes stable. It is suggested that the active principle evoking the contraction of the uterus may be a different substance from that which produces the characteristic pressor effect of pituitary extracts. H. W. B.

Influence of Protein Intake on Creatine Excretion in Children. W. DENIS and J. G. KRAMER with ANNA S. MINOT (*J. Biol. Chem.*, 1917, **30**, 189—196).—The results of feeding experiments on five children show that the amount of creatine found in the urine of children is directly dependent on the intake of protein, being high when large quantities of protein (creatine-free) are ingested, decreasing, and in some cases disappearing entirely, when the child is fed on a relatively low protein diet. Creatinuria in normal children is therefore due to the relatively high protein intake, which is the rule with practically all children. This condition is probably to be traced to the low saturation point of immature muscle for creatine revealed by the small creatine content of the muscles of children.

Since excessive protein katabolism in adults is attended with creatinuria (Denis, this vol., i, 496), and it has been shown that in pathological conditions urinary creatine is of exogenous origin (Denis, this vol., i, 367), it appears that the connexion between

creatinuria and protein metabolism is finally established (Folin and Denis, A., 1912, ii, 465). H. W. B.

Toxicity of Various Benzene Derivatives to Insects. WILLIAM MOORE (*J. Agric. Research*, 1917, **9**, 371—381).—Twenty-eight benzene derivatives (benzene, toluene, xylene and their chloro-, bromo-, iodo-, and nitro-derivatives, phenol, cresols, aniline, benzaldehyde, etc.) have been examined and compared with carbon disulphide as to their toxicity to the house-fly. Determinations were made of the different fractions of a gram-molecule necessary to kill in 400 minutes five flies enclosed in a stoppered litre flask with the compound. All the benzene derivatives tested were found to be more toxic to insects, molecule for molecule, than carbon disulphide. Although certain indications were found as to the relationship of chemical composition and toxicity, these were outweighed by the effect of physical properties. Up to 250°, the higher the boiling point the more toxic was the compound to insects. That the toxicity is not connected with lipoid solubility is shown by the fact that lipoids are very soluble in the compounds with low boiling points and but sparingly so in the compounds with high boiling points. For practical purposes, compounds with low boiling points, although less toxic, may give better results owing to their greater volatility. W. G.

The Sensitiveness of Strains of Nagana towards Arsenic and Antimony. ERNST TEICHMANN (*Biochem. Zeitsch.*, 1917, **81**, 284—318).—The author draws the following conclusions from a large amount of experimental material, which is given in detail. Different strains of *Nagana* obtained from East Africa show marked differences in their sensitivity to arsacetin when this drug is employed both prophylactically and therapeutically. One particular strain which has long been kept in European laboratories was quite insensitive to arsenic. This was also the case for derivatives of this strain which had become fast towards the anti-body. Similar differences in sensitivity were shown both by West and East African strains towards potassium antimonyl tartrate. In the case of this drug, the prophylactic treatment showed better results than the therapeutic. For curative treatment, arsacetin was more effective in the case of East African *Nagana* than potassium antimonyl tartrate. Each strain behaved differently, however, towards antimony and arsenic compounds as regards prophylactic and therapeutic action. There was no relationship between the virulence of a strain and its sensitivity towards the drugs. S. B. S.

Colloidal Nature of the Wassermann Reaction. R. M. WALKER (*J. Path. Bact.*, 1917, **21**, 184—192).—The author adduces evidence in support of the view that the fixation of complement is an adsorption by a colloidal complex formed from the antigen and the syphilitic serum. Normal serum does not confer

this property of selective adsorption on the antigen (compare Poyarkov, this vol., i, 427). G. B.

Comparison of the Actions of *d*-, *l*-, and *i*-Camphor. I. Toxicity to Cats. II. Action on the Frog's Heart. III. Antiseptic Action. GEORG JOACHIMOGLU (*Arch. exp. Path. Pharm.*, 1916—1917, **80**, 1—7, 259—281, 282—287).—In contradistinction to hyoscyamine, adrenaline, etc., there is no difference in the physiological action of the enantiomorphs. The investigation was suggested by the present shortage of *d*-camphor in Germany. G. B.

Peptone Hypoglycæmia. HUGH McGUIGAN and E. L. ROSS (*J. Biol. Chem.*, 1917, **30**, 175—179. Compare A., 1915, i, 1038).—The authors confirm previous results showing the production of hypoglycæmia in dogs after the intravenous injection of peptone solutions. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Nitrogenous Food Requirement of some of the Commoner Pathogenic Bacteria. M. H. GORDON (*J. Roy. Army Med. Corps*, 1917, **28**, 371—376).—Considerable differences exist. With dextrose as source of carbon, *B. coli*, *B. paratyphosus*, *B. pyocyaneus*, and *B. proteus* can satisfy their nitrogen requirements with ammonium salts and some of the simpler amides and amino-acids. *B. diphtheriae* and *B. pseudodiphtheriae*, Staphylococci, and Streptococci require more complex compounds. The cholera vibrio and *B. dysenteriae* can live on asparagine, but not on ammonium salts. G. B.

Improved Chemical Methods for Differentiating Bacteria of the Coli-aerogenes Family. WILLIAM MANSFIELD CLARK and HERBERT A. LUBS (*J. Biol. Chem.*, 1917, **30**, 209—234).—The classification of bacteria of the coli-aerogenes family by means of the Clark-Lubs methyl-red test is facilitated by using a medium containing 0·7% of anhydrous disodium hydrogen phosphate, 0·2% of potassium hydrogen phthalate, 0·1% of aspartic acid, and 0·4% of dextrose. H. W. B.

The Formation of Ferments. III. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **81**, 332—341).—In the first communication (this vol., i, 305) it was shown that *d*-glucose, *d*-galactose, and *d*- and *l*-arabinose contribute to the formation by bacteria of the urease ferment, whilst *d*-mannose and rhamnose are inactive. It

is now pointed out that in the case of the active sugars, the configuration $\begin{array}{l} \mathrm{OH}\quad \mathrm{H} \\ \dot{\mathrm{C}}\text{——}\dot{\mathrm{C}}\text{—CHO} \\ \dot{\mathrm{H}}\quad \dot{\mathrm{O}}\mathrm{H} \end{array}$ or the optical antipode exists, whereas in the case of the inactive sugars, the hydroxyl groups or hydrogen atoms are on the same side of the carbon atoms contiguous to the aldehyde group.

In continuation of the work described in the second communication (this vol., i, 430), it is now shown that the addition of edestin, but not of caseinogen, to Uschinski's medium promotes the formation of the urease. The addition of glycine, alanine, tyrosine, or valine was without effect. It has already been shown that addition of bouillon from horse-meat to Uschinski's medium promotes the formation of the urease. It was also found that culture on medium from certain bouillon tablets promotes ferment formation, and that the further addition of amino-acids accelerates this formation still more. The bouillon tablets also promote urease formation when added to Uschinski's medium. From the above-mentioned results, the conclusion is drawn that Uschinski's medium is wanting in amino-acids and some other substance which is contained in the bouillons and in the hydrolysis products of edestin. Further experiments showed that synthetic leucine had no effect on urease formation when added to Uschinski's medium, whereas pure *l*-leucine, and *d*- and *l*-*iso*leucine (obtained from F. Ehrlich), promoted the formation of the ferment. It has therefore been found possible to obtain the ferment when bacteria are grown on media containing only simple chemical substances. It is not clear from the author's statements why synthetic leucine is inactive. S. B. S.

The Significance of Nitrification as a Factor in Soil Fertility. P. L. Gainey (*Soil Sci.*, 1917, **3**, 399—416).—A very full résumé of the literature on the subjects of (*a*) the existence of active nitrifying organisms in cultivated soils, (*b*) the relation between ammonia content and nitrifying power of soils, (*c*) the relation between ammonia nitrogen content and crop yield. Certain new experimental data are given, and the author draws the general conclusion that whilst nitrification is perhaps a valuable and even essential asset in fertility, it probably does not, under normal conditions, become a limiting factor in productivity. W. G.

The Extraction and Saturation of Soils with Volatile Antiseptics. J. P. du Buisson (*Soil Sci.*, 1917, **3**, 353—392).—Two soils, both heavy loams, were subjected to partial sterilisation with the following antiseptics: alcohol, benzene, ether, toluene, and gasolene (light petroleum). The treatment was carried out in two ways: (1) by extracting the soils with the antiseptics, and (2) by merely saturating them, the soils being in both cases subsequently freed from the antiseptics by exposure to air. Pot

cultures of wheat and oats showed that all the above substances except gasolene could be used satisfactorily for partial sterilisation, alcohol giving the best results; also, that although the beneficial effect of sterilisation was still evident on a second crop, it was greatly diminished and varied somewhat with the nature of the soil under investigation. Portions of the same soils were incubated for a period of six months, and analysed for ammonia and nitric acid at intervals. Sterilisation inhibited nitrification and increased ammonification for a certain length of time, after which ammonification either decreased or remained constant, whilst nitrification became more active than in the untreated soil. Nitrification and ammonification tests carried out on the soils after they had been cropped once and twice confirmed the conclusion drawn from the pot experiments, and showed that the effect of sterilisation on the two above processes practically ceased after the first crop. Breaking up the soil and maintaining it in a loose condition did not increase the amount of ammonia and nitric nitrogen in the soil.

From the alcohol extracts of the soils a substance was recovered which proved toxic in water cultures. Extracted soils, however, did not give better results than saturated soils; in fact, the latter more usually yielded the larger plants. L. M. U.

Amygdalin as Nutriment for Aspergillus niger. II. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 987—989. Compare this vol., i, 502).—Further experiments on the influence of amygdalin on the development of *Aspergillus niger* show conclusively that amygdalin is absorbed by the organism without any previous resolution into dextrose, benzaldehyde, and hydrogen cyanide. The experiments show that amygdalin diminishes the noxious influence of benzaldehyde. H. M. D.

Influence of Mineral Matters on the Germination of Peas. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1917, **165**, 45—51. Compare *ibid.*, **164**, 979).—Peas were germinated on sand moistened with water containing varying amounts of the salts examined, which were the chlorides of sodium, potassium, strontium, barium, manganese, and lead, and the sulphates of ammonium, calcium, magnesium, zinc, aluminium, and copper. The seeds were steeped for twenty-four hours and then allowed to germinate for six days, after which the length of the roots formed were measured. Calcium appears to be the only metal exerting any marked influence on the germination, the root length being markedly increased by the presence of as little as 0·01 mg. of calcium sulphate for each seed. As the amount of calcium salt is increased, the length of the root increases and the root hairs become more abundant. After calcium come strontium, manganese, aluminium, barium, and magnesium. Then come the alkali metals, zinc, lead, and copper, which has no immediate effect at the low concentrations, but appears to be toxic at a concentration of 0·1 mg. of anhydrous copper sulphate per seed. W. G.

Lævulose the Preponderant Sugar of Apple Juices. JOHN R. EOFF, jun. (*J. Ind. Eng. Chem.*, 1917, **9**, 587—588).—An examination of the relative proportions of sucrose, dextrose, and lævulose in the juices of twenty varieties of apples by a polarimetric method (Thompson and Whittier, Delaware Coll. Agric. Expt. Stat., 1913, Bull. 102) and a combined polarimetric-reducing power method (Browne, A., 1906, ii, 498). The results indicate that in every case the amount of lævulose exceeds the total quantity of other sugars present and confirms the earlier observations of Thompson and Whittier (*loc. cit.*), of Browne (A., 1902, ii, 371), and of Worcollier (*Ann. Falsif.*, **2**, 425). D. F. T.

Secretions in the Rhizome of Rheum; a Contribution to the Microchemistry of the Hydroxymethylanthraquinone-bearing Plants. O. TUNMANN (*Ber. Deut. bot. Ges.*, 1917, **35**, 191—203).—It not infrequently happens that when the rhizomes of Chinese rhubarb are split open, large, tumour-like growths are found imbedded in the normal tissue, separated completely by a layer of cork. Under what conditions these abnormal deposits are produced cannot be answered except by experiments on the living plant, but it is unlikely that the first cause is the boring in of insects. The author has, however, been able to determine the chief differences between the normal tissue and the enclosed growth, having at his disposal a specimen in which there were two such deposits, one inside the other, each bounded by cork tissue, the larger being nearly 5 cm. long.

The secretions consist of complex tissues which are practically free from starch, uncombined or glucosidic sugars, but rich in the usual oxalate druses. As the starch-bearing parenchyma is empty, this tissue is greatly compressed, and the oxalate cells appear to be abnormally numerous. Catechol and gallic acid are present in the woody fibres in undiminished quantity. Likewise, the residues of the anthraquinone-glucosides, namely, the hydroxymethylanthraquinones, are present in large quantities, but largely as the corresponding anthranols. These reduction products can be obtained by micro-sublimation, and recognisable nitro-compounds of the hydroxymethylanthraquinones can also be prepared on a microscope slide by warming a section of the growth with pure nitric acid. J. C. W.

Action of Coal Gas on Plants. II. Action on Green Plants. C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, **35**, 318—332. Compare this vol., i, 507).—It is usually affirmed that coal gas is poisonous to green plants even when the atmosphere contains only minute quantities, but cress is remarkably resistant to its influence. The seedlings will grow unchecked in an atmosphere containing as much as 30% of gas, but they die in a short time if exposed to undiluted gas. The seeds themselves are not killed by coal gas, but only prevented from germination. The ill-effects of pure coal gas are not entirely due to the lack of oxygen, for cress will keep fresh and green in pure hydrogen for a much longer time than in coal gas. Experiments designed to elucidate the nature of the

particularly poisonous constituent of coal gas gave only negative results. Carbon monoxide, ethylene, and acetylene are not dangerous, even in concentrations much higher than those in which they commonly occur in coal gas. Benzene vapour, carbon disulphide, and hydrogen sulphide are very toxic, but not in the concentration met with in coal gas. The really toxic constituent is probably among the minor impurities. J. C. W.

The Aldehydes of Wines. J. LABORDE (*Ann. Inst. Pasteur*, 1917, **31**, 215—252).—A comprehensive study of the catalytic and physiological agents causing aldehyde formation in wines. These agents exercise their influence principally on the young wines during their storage in barrels, which helps more or less the contact of the wine with atmospheric oxygen. The three principal catalytic agents promoting aldehyde formation are: (1) the tannin substances, more or less combined with potassium hydroxide; (2) œnoxydase; (3) the oxydase of *Botrytis cinerea*. Pasteurisation of normal wines, as well as the addition of sulphurous acid, checks aldehyde formation without completely preventing it. Pasteurisation behaves similarly with "cassable" wines, but in this case sulphurous acid favours aldehyde formation, whilst preventing the "casse." There are equally important opposing influences which may lead to the complete disappearance of aldehyde from the wine if it is stored in the absence of air, and on this account but small amounts of aldehydes are to be found in red wines stored normally. In the case of "cassable" wines, the aldehyde plays no part, since it is only formed after marked oxidation of the tannin substances. Aldehyde formation opposed by aldehyde destruction has only a passing influence, although always unfavourable, on the bouquet of red wines in casks.

Of the micro-organisms which live in wine, only the facultative aerobic organisms (different yeasts) and the strictly aerobic organisms (mycoderma) produce aldehyde, although certain anaerobic ferments apparently yield acraldehyde by attacking the glycerol of the wine. The yeasts and anaerobic microbes secrete reductases in the wine, which can contribute to the complete removal of aldehydes in wine, kept out of contact with air, unless the aldehydes are combined with sulphurous acid. W. G.

Investigation of Soil Excrescences. H. PUCHNER (*Kolloid Zeitsch.*, 1917, **20**, 209—238).—The author discusses the formation of salt layers on the surface of various natural or artificial substances as the result of weathering, the immediate cause of the production of these efflorescences or excrescences being the removal of water by evaporation.

Experiments are described which show that the growth of these superficial layers is very appreciably influenced by the nature of the soil or other substance in which the salt is present. The general appearance and the crystalline structure of the separated salt is not only affected by the presence of colloidal humus substances, but also by the fineness of the soil particles. H. M. D.

Organic Chemistry.

Action of Anhydrous Aluminium Chloride [and Ferric Chloride] on Unsaturated Organic Compounds. II. WILMER C. GANGLOFF and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1420—1427. Compare A., 1916, i, 593).—Further compounds of aluminium and ferric chlorides with unsaturated hydrocarbons, acids, alcohols, and aldehydes are described, and their bearing on the use of these catalysts in the cracking of petroleum is discussed.

Acetylene gives the *compounds* $AlCl_3,C_2H_2,2EtOH$ and $AlCl_3,C_2H_2,MeOH,H_2O$; ethylene forms the *compounds* $AlCl_3,C_2H_4,2EtOH$ and $AlCl_3,C_2H_4,MeOH,H_2O$; γ-butylene yields the granular *product* $AlCl_3,CMe_2\!:\!CH_2,2MeOH,H_2O$; β-*iso*amylene gives a series of bright-coloured tars according to the amount of aluminium chloride, but an alcoholic solution yields the crystalline *compound* $AlCl_3,CMe_2\!:\!CHMe,MeOH$; styrene forms the sweet-smelling compounds $AlCl_3,C_8H_8$ and $AlCl_3,2C_8H_8,2H_2O$.

Oleic acid forms an asphalt-like mass, but if diluted with methyl alcohol, a *compound*, $4AlCl_3,C_{18}H_{34}O_2$, resembling brown sugar, may be isolated. Fumaric acid yields a snow-white *compound*, $AlCl_3,C_4H_4O_4$, which sublimes unchanged at 200°. A methyl-alcoholic solution of furfuraldehyde gives a crystalline, coal-like *product*, $AlCl_3,C_5H_4O_2,MeOH$, and a solution of benzaldehyde forms a pale yellow, crystalline *compound*, $AlCl_3,C_7H_6O,MeOH$. Diluted allyl alcohol yields the pungent-smelling *compound* $AlCl_3,C_3H_6O,MeOH$.

Anhydrous ferric chloride reacts with methyl-alcoholic solutions of amylene and furfuraldehyde to form the *compounds* $FeCl_3,C_5H_{10},MeOH$ and $FeCl_3,C_5H_4O_2,MeOH$ respectively.

The yields of benzophenone obtained in the condensation of benzoyl chloride with benzene under the influence of various anhydrous metallic chlorides have been roughly determined. Under similar conditions, aluminium chloride gave 70—71%, ferric chloride 60—62%, zinc chloride 28—32%, chromic and cuprous chlorides nil. J. C. W.

Preparation of Ethylene Glycol. BENJAMIN T. BROOKS and IRWIN HUMPHREY (*J. Ind. Eng. Chem.*, 1917, **9**, 750—751).—One mol. of ethylene dichloride, 5 volumes of methyl alcohol, and 3 mols. of sodium formate are heated together at 165° to 170° in an autoclave for seven hours. After cooling, the methyl alcohol solution is separated from the salts and distilled. The methyl alcohol may be distilled at ordinary pressure and the glycol under reduced pressure. Ethylene dichloride is readily prepared by the action of chlorine on ethylene at 0°; if the mixture becomes heated, large quantities of trichloroethane are formed. The gases should not be dried. W. P. S.

Preparation of β-Chloro- and β-Bromopropionic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1465—1466).—Ethylene chlorohydrin is dissolved in alcohol, concentrated potassium cyanide solution is gradually added to the boiling solution, and after some hours the cyanohydrin is isolated and distilled (b. p. 110°/15 mm.). On hydrolysis with hydrochloric or hydrobromic acid, β-chloro- or β-bromopropionic acid is obtained in good yield, replacement of the hydroxyl group by halogen taking place simultaneously.

J. C. W.

Hydrogen Oxalates of the Alkali Earth Metals. G. BRUHNS (*Zeitsch. anorg. Chem.*, 1916, **95**, 194—224).—In view of the uses of oxalic acid in analysis, and of the advantages of pure oxalic acid as a standard for volumetric solutions (A., 1916, ii, 158, 533), the conditions under which acid salts of the alkali earths are formed have been investigated.

Dilute solutions of barium chloride yield with 2 mols. of oxalic acid a crystalline precipitate of the salt $BaH_2(C_2O_4)_2,2H_2O$, which is rapidly decomposed by cold water. $1H_2O$ is readily lost, even at atmospheric temperature in a vacuum, whilst the other molecule is only driven off at 125°. Solutions of progressively diminishing acidity yield the salts $Ba_2H_2(C_2O_4)_3,3H_2O$ and

$$Ba_3H_2(C_2O_4)_4,3H_2O,$$

all being similar in appearance.

Titration with *N*/10-sodium hydroxide shows that a small part of the oxalic acid remains combined with the normal oxalate, even after prolonged boiling. When barium hydroxide solution is in excess, the precipitated barium oxalate contains an excess of barium. The error in titrating barium with oxalic acid, and conversely, is therefore considerable.

Normal barium oxalate may contain more than $1H_2O$ when precipitated cold from barium hydroxide and oxalic acid, whilst the product from barium chloride and sodium oxalate may contain less than 1 mol., even from dilute solution. At 100° it only contains $\frac{1}{2}H_2O$.

Strontium has less tendency to form acid salts. A salt, $Sr_2H_2(C_2O_4)_3,2H_2O$, is obtained which is decomposed completely by cold water. Slow crystallisation from slightly acid solution, however, yields homogeneous crystals containing an excess of acid which are only very slowly decomposed by water. Strontium chloride is more suitable than calcium chloride for addition in the titration of oxalic acid under conditions which cause rapid precipitation. A *N*/10-solution of strontium hydroxide is very suitable for volumetric estimations of oxalic acid, care being taken that the alkaline solution is not in excess, which would cause the precipitate to retain strontium. The water of crystallisation varies, as in the case of other oxalates, with the conditions of preparation.

The titration of oxalic acid in nitric acid solution is quite satis-

factory in the presence of barium nitrate, and even of barium chloride. C. H. D.

The System Water–Uranyl Oxalate–Ammonium Oxalate. A. Colani (*Compt. rend.*, 1917, **165**, 234—236).—An examination of the solubility curves of the system water–uranyl oxalate–ammonium oxalate at 15°, 50°, and 75° confirms the results of Rosenheim and Lienau (compare A., 1899, i, 569) and Wyrouboff (compare *Bull. Soc. Franc. Min.*, 1909, **32**, 351) as to the existence of the complex $(NH_4)_2(UO_2)(C_2O_4)_2,2H_2O$, and of Wyrouboff (*loc. cit.*) of the complex $(NH_4)_4(UO_2)(C_2O_4)_3$, and in addition indicates the existence of a new *compound*,

$$(NH_4)_2(UO_2)_2(C_2O_4)_3,3H_2O.$$

At 50° only the anhydrous salts are formed, and the salt $(NH_4)_4(UO_2)(C_2O_4)_3$ is only formed at 60° or above. W. G.

Oxidation of the Alkali Butyrates by Hydrogen Peroxide with the Production of Succinic Acid. Edward Cahen and William Holdsworth Hurtley (*Biochem. J.*, 1917, **11**, 164—171).—When sodium butyrate and hydrogen peroxide in aqueous solution are heated together at 65°, succinic acid is produced, and may amount to as much as 50% of the oxidised butyrate. When the amount of hydrogen peroxide is relatively increased, the yield of succinic acid is diminished, whilst that of carbon dioxide is enormously increased. Under the conditions observed, the fatty acid is attacked at the methyl group at the end of the carbon chain instead of at the α- and β-carbon atoms, as found in the experiments of Dakin (A., 1908, i, 74).

H. W. B.

Crystallographic Investigations of the Succinic Acids, their Homologues and Derivatives. Anton Stefl (*Zeitsch. Kryst. Min.*, 1914, **54**, 343—387).—The object of this work was to investigate the crystallographic relationships between geometrically isomeric acids and their derivatives. It has also been extended to include the glutaric and mesaconic acids and their derivatives.

Succinic acid forms monoclinic plates or prisms, varying in habit according to the solvent, water, acetone, ethyl acetate, etc. [$a:b:c=0.5747:1:0.8581$; $\beta=133°37'$]. Cleavage and optic axial plane, {010}; D 1·577; M.V. 74·81.

cis-s-Dimethylsuccinic acid, monoclinic prisms from water or ethyl acetate [$a:b:c=0.6967:1:0.8549$; $\beta=93°9\frac{1}{2}'$]; D 1·349(7); M.V. 110·69. Cleavage and optic axial plane, {010}.

trans-s-Dimethylsuccinic acid, triclinic plates from ether [$a:b:c=0.8485:1:0.8944$; $\alpha=97°54\frac{1}{2}'$; $\beta=125°9\frac{1}{2}'$; $\gamma=89°47\frac{1}{2}'$]. Cleavage plane, {010} perfect; {$\bar{1}10$} and {$1\bar{1}0$} less good. D 1·349; M.V. 110·72.

as-Dimethylsuccinic acid, prepared by Bone and Sprankling's method (T., 1899, **75**, 858), forms triclinic prisms from acetone

[$a:b:c=1·1265:1:2·0244$; $\alpha=78°40'$; $\beta=105°30'$; $\gamma=112°8\frac{1}{2}'$]. Cleavage, {010} and {110}; D 1·323; M.V. 110·38.

Trimethylsuccinic acid, rhombic prisms from water, alcohol, ether, or amyl acetate [$a:b:c=0·6585:1:0·8297$]. Cleavage {010} and {110}; optic axial plane {100}; D 1·242(5); M.V. 128·77.

Tetramethylsuccinic acid, from ether or acetone, forms both monoclinic and triclinic crystals; from aqueous methyl alcohol, light petroleum, or ethyl acetate only triclinic.

Monoclinic form: [$a:b:c=1·0923:1:0·7208$; $\beta=100°26'$]; cleavage {100} and {010}; D 1·300; M.V. 133·85.

Triclinic form: [$a:b:c=0·7556:1:2·0168$; $\alpha=89°42'$; $\beta=101°39'$; $\gamma=89°33'$]; cleavage {110} and {$1\bar{1}0$}; D 1·300.

n-s-Dimethyldiethylsuccinic acid, triclinic prisms, pseudo-hexagonal with respect to the axis *b*, from acetone solution [$a:b:c=0·8499:1:0·8954$; $\alpha=97°50'$; $\beta=124°25'$; $\gamma=90°0'$]; cleavage perfect on {010}, poor on { 01 }; D 1·247; M.V. 161·95.

Glutaric acid, thin, monoclinic, six-sided plates from acetone [$a:b:c = 2·0737:1:3·5359$; $\beta = 131°36'$]; cleavage {100} and {110}; optic axial plane {010}; D 1·427; M.V. 92·50.

Mesaconic acid, thin, four-sided plates from ether, monoclinic (sphenoidal?) [$a:b:c=0·5933:1:1·2632$; $\beta=108°34'$]; cleavage {100}; optic axial plane {010}; D 1·466; M.V. 88·68.

Tetramethylsuccinodinitrile, monoclinic plates from ether, alcohol, etc. [$a:b:c=0·6890:1:0·7109$; $\beta=116°25'$]; cleavage and optic axial plane, {010}; D 1·070; M.V. 127·1.

s-Dimethyldiethylsuccinodinitrile, triclinic plates [$a:b:c=0·4947:1:0·5913$; $\alpha=99°54'$; $\beta=110°41\frac{1}{2}'$; $\gamma=89°7\frac{1}{2}'$]; D 1·075(5); M.V. 152·5.

Tetraethylsuccinodinitrile, triclinic plates [$a:b:c=0·5109:1:1·1998$; $\alpha=80°2'$; $\beta=110°45'$; $\gamma=90°40'$]; D 1·076; M.V. 178·46.

Succinic anhydride, stable crystalline modification, forms rhombic, bipyramidal prisms [$a:b:c=0·5945:1:0·4603$]. Cleavage and glide plane, {101}; optic axial plane, {001}; D 1·503; M.V. 66·54.

cis-s-Dimethylsuccinic anhydride, monoclinic plates [$a:b:c=0·5859:1:1·6044$; $\beta=93°31'$]; D 1·337; M.V. 95·75.

Measurable crystals of the trans-isomeride of *as*-dimethylsuccinic and tetramethylsuccinic anhydrides could not be obtained.

s-Dimethyldiethylsuccinic anhydride, monoclinic prisms [$a:b:c=0·5900:1:0·9756$; $\beta=91°29\frac{1}{2}'$]; D 1·189; M.V. 154·7.

Tetraethylsuccinic anhydride, stout, monoclinic crystals from ether, alcohol, ethyl acetate, etc. [$a:b:c=0·8842:1:0·9052$; $\beta=95°34\frac{1}{2}'$]; D 1·207(8); M.V. 175·53.

Glutaric anhydride, long, flat, monoclinic prisms from ether [$a:b:c=1·4249:1:1·9623$; $\beta=91°47'$]; D 1·411; M.V. 80·81.

Succinimide, stable modification, rhombic, bipyramidal plates or prisms from acetone [$a:b:c=0·7888:1:1·3655$]; D 1·418; M.V. 71·42.

cis-s-Dimethylsuccinimide, thin, monoclinic plates [$a:b:c=0·9089:1:1·3153$; $\beta=100°10\frac{1}{2}'$]; cleavage, {001}; optic axial plane perpendicular to {010}; D 1·284; M.V. 98·91. The crystals of the trans-isomeride could not be measured.

as-Dimethylsuccinimide, six-sided, tabular, monoclinic crystals from ethyl acetate or alcohol [$a:b:c=2·0385:1:1·8937$; $\beta=120°37'$]; cleavage, {001}; optic axial plane, {010}; D 1·244; M.V. 102·04.

Trimethylsuccinimide, rhombic prisms, a combination of a rectangular prism with basal plane. The axial ratios could not be determined.

Tetramethylsuccinimide, thin, monoclinic plates or needles [$a:b:c=1·6255:1:2·0679$; $\beta=92°8'$]; D 1·185; M.V. 130·76.

s-Dimethyldiethylsuccinimide, monoclinic prisms [$a:b:c=0·5829:1:0·9773$; $\beta=91°32'$]; D 1·189(9); M.V. 153·79.

Tetraethylsuccinimide, triclinic tables [$a:b:c=0·8549:1:1·4893$; $\alpha=79°16'$; $\beta=105°52'$; $\gamma=86°55'$]; D 1·166; M.V. 180·99.

Glutarimide, rectangular, monoclinic tables from alcohol or ethyl acetate [$a:b:c=0·9849:1:1·3772$; $\beta=102°17'$]; cleavage, {001} and {100}; D 1·393; M.V. 81·12.

Citraconimide, monoclinic plates [$a:b:c=?:1:1·3154$; $\beta=100°0'$]; cleavage, {100}; D 1·410; M.V. 78·72.

Succinochloroimide, rhombic plates (? bipyramidal) [$a:b:c=0·8949:1:1·6308$]; optic axial plane, {100}; D 1·650; M.V. 80·72.

Succinobromoimide, rhombic bisphenoidal crystals [$a:b:c=0·8994:1:1·6360$]; axial plane, {100}; D 2·098; M.V. 84·7.

Succinoiodoimide, ditetragonal bipyramidal [$a:c=1:0·8733$]; D 2·245; M.V. 100·16.

Tetramethylsuccinochloroimide, four-sided rhombic bipyramidal plates [$a:b:c=0·9848:1:1·3912$]; optic axial plane, {010}; D 1·303; M.V. 145·19.

Tetramethylsuccinobromoimide, isomorphous with the last [$a:b:c=0·9898:1:1·4650$]; optic axial plane, {100}; D 1·578; M.V. 147·88.

Tetramethylsuccinoiodoimide, rhombic pyramidal [$a:b:c=1·1051:1:0·8502$]; D 1·816; M.V. 154·69.

Succinanil, monoclinic tables [$a:b:c=2·1125:1:2·3065$; $\beta=101°42'$]; cleavage, {100}; optic axial plane, {010}; D 1·356; M.V. 129·75.

cis-s-Dimethylsuccinanil, rhombic bipyramidal prisms [$a:b:c=1·2568:1:2·6730$]; cleavage, {001}; D 1·253; M.V. 161·97.

trans-s-Dimethylsuccinanil, monoclinic plates [$a:b:c=1·3724:1:3·0810$; $\beta=116°17'$]; cleavage, {001}; optic axial plane, {010}; D 1·239; M.V. 163·84.

as-Dimethylsuccinanil, monoclinic needles [$a:b:c=2·3885:1:4·1003$; $\beta=97°1'$]; cleavage, {001}; optic axial plane, {010}; D 1·247; M.V. 162·73.

Trimethylsuccinanil, rhombic bipyramidal prisms [$a:b:c=1·6490:1:2·3204$]; cleavage, {001}; optic axial plane, {010}; D 1·240; M.V. 175·0.

Tetramethylsuccinanil, long, monoclinic prisms [$a:b:c=3\cdot2444:1:6\cdot3002$; $\beta=90°37'$]; cleavage, {001}; D 1·199; M.V. 192·58.

s-Dimethyldiethylsuccinanil, monoclinic prisms [$a:b:c=1\cdot2882:1:2\cdot4242$; $\beta=93°17\frac{1}{2}'$]; D 1·181; M.V. 219·3.

Glutaranil, monoclinic tables [$a:b:c=2\cdot4120:1:2\cdot4318$; $\beta=97°37'$]; cleavage, {100}; optic axial plane, {010}; D 1·304; M.V. 144·88.

Citraconanil, monoclinic thin needles or plates [$a:b:c=2\cdot7652:1:2\cdot8700$; $\beta=99°36'$]; optic axial plane, {010}; D 1·283; M.V. 145·75.

Those compounds having a cyclic structure show much closer crystallographic relationship among themselves than those having open-chain structures. There is not generally the close relationship between anhydrides and imides which might have been expected, but these derivatives of *s*-dimethyldiethylsuccinic acid are isomorphous. The entrance of a CH_3 group occasions less morphotropic change in the cyclic than in the open structures. Morphotropic relationships are clear among some of the halogen imides and among the anils. E. H. R.

Two Isomeric Citronelaldehydes. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 692—695).—By repeated fractionation, two isomerides have been isolated from citronelaldehyde. The first has b. p. 203—204°, D^{14} 0·8880, and forms a semicarbazone, m. p. 85—86°. The second has b. p. 198—200°, D^{14} 0·8745, and gives a semicarbazone, m. p. 82·5—83°. It is suggested that the first has the formula $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$, and the second the formula $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$. A. J. W.

The Influence of Constitution on the Rotation of Optically-active Substances. X. Optically-active Ketones and Diketones. H. RUPE and SAMUEL WILD (*Annalen*, 1917, **414**, 111—125).—As it is possible to obtain many saturated and unsaturated derivatives of ketones and aldehydes, the influence of constitution on the optical properties of active members of these classes can be investigated most advantageously. Not much is known concerning optically active ketones and aldehydes, but a beginning has now been made with derivatives of amylacetone (ε-methylheptan-β-one).

Ethyl amylacetoacetate, prepared from active amyl bromide and ethyl sodioacetoacetate, has b. p. 112°/10 mm., D_4^{20} 0·9513, $[\alpha]_D^{20}$ +13·66°, 14·11° in 10% benzene solution. The "characteristic wave-length," λ_a (see A., 1915, ii, 718) is 643·0 for the pure liquid and 592·3 for the 10% benzene solution. The inactive ester has the same b. p. Active *amylacetone* [*ε-methylheptan-β-one*] is obtained by hydrolysis with 12% methyl-alcoholic potassium hydroxide as a mobile oil, resembling amyl acetate; b. p. 70°/11 mm., D_4^{20} 0·8295, $[\alpha]_D^{20}$ +8·20°, 7·34° in 10% benzene, 8·09° in 10% alcohol, λ_α 664·2, 581·9 for benzene solution, 609·8 for alcoholic solution. The ketone condenses with benzaldehyde in the presence of sodium hydroxide to yield *benzylideneamylacetone* [*α-benzyl-*

idene-ε-methylheptan-β-one]; the *active* form crystallises in matted, silvery-white needles, m. p. 138°, $[\alpha]_D^{20}$ +10·77°, λ_a 547·9 for 10% solution in benzene; the *inactive* form has m. p. 173°. The corresponding *anisylidene* compound crystallises in large, pearly scales; the *active* form has m. p. 55°, $[\alpha]_D^{20}$ +8·62°, λ_a 547·7 for 10% solution in benzene; the *inactive* form has m. p. 93°. The ketone also condenses with ethyl acetate under the influence of sodium and with ethyl benzoate in the presence of sodamide; active *acetylamylacetone* [*η-methylnonan-βδ-dione*],

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMeEt$,

is a pale yellow, viscous oil, b. p. 103°/10 mm., D_4^{20} 0·9202, $[\alpha]_D^{20}$ +9·80°, 8·28° in 10% benzene, λ_a 630·0, 579·7 in benzene solution, and forms a pale green copper salt; active *benzoylamylacetone* [*α-phenyl-ζ-methyloctan-αγ-dione*] is a pale yellow, aromatic oil, b. p. 106—107°/0·1 mm., 180°/10 mm., D_4^{20} 1·005, $[\alpha]_D^{20}$ +9·41°, 6·87° in 10% benzene, 6·44° in 10% solution in 10% sodium hydroxide, λ_a 620·0, 580·0 in benzene, 587·7 in sodium hydroxide, and it forms a pale green copper salt.

Some menthyl derivatives were prepared for comparison with these. Menthyl acetoacetate has b. p. 149·5°/10·25 mm., D_4^{20} 0·9866, $[\alpha]_D^{20}$ −69·21°, 69·32° in 10% benzene, λ_a 678·9, 698·7 in benzene. The sodium compound of this reacts with α-bromoethylbenzene to form *menthyl α-phenylethylacetoacetate* (*menthyl α-acetyl-β-phenylbutyrate*), $CHMePh{\cdot}CHAc{\cdot}CO_2{\cdot}C_{10}H_{19}$, as a thickly matted mass of slender needles, m. p. 98°, b. p. 217°/11 mm., $[\alpha]_D^{20}$ +108·16°, λ_a 635·2, for 10% solution in benzene. [The corresponding *ethyl* ester has b. p. 154°/11 mm.] This may be hydrolysed to *δ-phenylpentan-β-one*, b. p. 109—110°/11 mm. Menthyl sodioacetoacetate also reacts with active amyl bromide to form *menthyl amylacetoacetate*, b. p. 185°/10 mm., D_4^{20} 0·9723, $[\alpha]_D^{20}$ −40·48°, λ_a 698·8.

The rotations for the *C*, *E*, and *F* lines, and the values of $[\alpha]_F/[\alpha]_C$ and $[\alpha]_F-[\alpha]_C$ are also given.

With the exception of the menthyl derivatives, it will be seen that the highest rotatory power is possessed by the active ethyl amylacetoacetate, in which the asymmetric grouping is bounded by two carbonyl groups. With only one carbonyl group, as in amylacetone, the rotatory power is much less, but is still higher than that of amyl alcohol, and the rotation is almost as low if the two carbonyl groups are not near the asymmetric carbon atom, as in the two acylamylacetones. The "characteristic wave-lengths," λ_a, for the pure compounds vary considerably, but the values for the solutions are about the same. Certain constitutional differences must therefore disappear on dissolving the compounds, and the effect of the solvent on the rotation–dispersion is consequently very pronounced. J. C. W.

Some New Compounds of Dextrose. P. Karrer (*Ber.*, 1917, **50**, 833—837. Compare A., 1916, i, 832).—By the interaction of bromoacetoglucose and the silver salt of an organic acid in an

inert solvent, tetra-acetyl derivatives of the corresponding ester of dextrose have been obtained. Unfortunately, it has not been found possible to eliminate the acetyl radicles without simultaneously removing the organic acid group, so that the influence of the dextrose molecule on the physiological activity of the acids employed could not be observed.

In boiling toluene, silver 2-phenylquinoline-4-carboxylate and bromoacetoglucose react with the formation of *tetra-acetyldextrose 2-phenylquinoline-4-carboxylate*, $N{<}{\genfrac{}{}{0pt}{}{C_6H_4}{CPh{\cdot}CH}}{>}CO_2{\cdot}C_6H_7O_5Ac_4$, needles, m. p. 151°, which on treatment with methyl-alcoholic ammonia yields *2-phenylquinoline-4-carboxylamide*, $C_{16}H_{12}ON_2$, needles, m. p. 196°.

Under similar conditions, bromoacetoglucose and silver salicylate react, giving rise to two isomeric substances, namely. *tetra-acetyldextrose salicylate*, $OH{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_6H_7O_5Ac_4$, crystals, m. p. 185°, and *salicylic acid tetra-acetylglucoside*, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_7O_5Ac_4$, a lævorotatory substance, m. p. 167°. The former gives a violet coloration with ferric chloride, and with methyl-alcoholic ammonia yields salicylamide, whereas the latter gives no coloration and is soluble without fission in very dilute aqueous ammonia, whilst on hydrolysis with alkalis or more concentrated ammonia it yields salicylic acid. The formation of these two isomerides is attributed to the co-existence of two modifications of silver salicylate, namely,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO_2Ag}{OH}} \quad \text{and} \quad C_6H_4{<}{\genfrac{}{}{0pt}{}{CO_2H}{OAg}}$$

D. F. T.

Synthesis of Disaccharides containing Sulphur and Selenium. WILHELM SCHNEIDER and FRITZ WREDE (*Ber.*, 1917, **50**, 793—804. Compare Schneider and others, A., 1916, i, 791, 792; 1914, i, 669, 977).—The interaction of β-bromoacetylglucose and potassium hydrogen sulphide in alcoholic solution gives rise to an uncrystallisable substance, together with the *octa-acetate*, $C_{28}H_{38}O_{18}S$, colourless needles, m. p. 174°, $[\alpha]_D^{25}$ $-38{\cdot}21°$ in *s*-tetrachloroethane, of a disaccharide containing an atom of sulphur. This product probably owes its formation to the presence of normal potassium sulphide in the alcoholic solution. By treatment with a methyl-alcoholic solution of ammonia (Fischer and Helferich, A., 1914, i, 333), the octa-acetate was convertible into the corresponding thio-disaccharide, $C_{12}H_{22}O_{10}S$, hexagonal leaflets, m. p. 174°, $[\alpha]_D^{23}$ $-84{\cdot}78°$ in water, to which, from its apparent analogy with *iso*trehalose (Fischer and Delbruck, A., 1909, i, 633), is given the name *thio*iso*trehalose*. Thio*iso*trehalose is remarkably resistant to hydrolytic agents; it is indifferent to warm aqueous alkalis, whilst mineral acids liberate hydrogen sulphide only slowly even in hot concentrated solution; emulsin, yeast enzyme (Lebedeff, A., 1911, i, 248, 828), trehalase, and myrosin are without action. From the fact that Fehling's solution is not reduced, it is probable that thio*iso*trehalose does not contain an aldehydic group. Thio*iso*trehalose

gives a *potassium* derivative, $C_{12}H_{21}O_{10}SK,2H_2O$, microscopic needles, decomp. at 170—180°, and a *dipotassium* derivative,

$C_{12}H_{20}O_{10}SK_2,4H_2O$,

microscopic tetragonal double pyramids, decomp. near 170°.

In a similar way, using an alcoholic solution of potassium selenide, it was possible to obtain an *octa-acetylseleno*iso*trehalose*, $C_{28}H_{38}O_{18}Se$, colourless needles, m. p. 186°, $[\alpha]_D^{21}$ −51·24° in *s*-tetrachloroethane, which on hydrolysis with methyl-alcoholic ammonia gave *seleno*iso*trehalose*, $C_{12}H_{22}O_{10}Se$, crystals closely resembling the corresponding thio-compound, m. p. 193°, $[\alpha]_D^{26}$ −83·58° in water; *potassium* derivative, $C_{12}H_{21}O_{10}SeK,2H_2O$, needles, decomp. near 132°; *dipotassium* derivative, $C_{12}H_{20}O_{10}SeK_2,4H_2O$, tetragonal, double pyramids, decomp. near 130°. Like the thio-analogue, seleno*iso*trehalose is a sweet substance of remarkable resistance to hydrolysis and mild oxidising agents. Not only are these compounds unaffected by the hydrolytic agents mentioned above, but when administered to dogs or guinea-pigs they are eliminated unaltered in the urine. D. F. T.

Bromoethylamine. S. GABRIEL (*Ber.*, 1917, **50**, 826—827).—Bromoethylamine is prepared most conveniently by saturating at 0° with hydrogen bromide a mixture of aminoethyl alcohol and fuming hydrobromic acid, the resulting mixture being heated for one hour at 170°; the m. p. of bromoethylamine hydrobromide is 172·5—173·5°, and not 155—160°, as stated previously.

When hydroxyethylcarbamide is heated with fuming hydrobromic acid solution at 100° for one hour the product is unstable *bromoethylcarbamide*, $CH_2Br\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, needles, m. p. 91°, which on being kept for several days undergoes transformation into ethylene-ψ-carbamide hydrobromide, $\begin{matrix}CH_2\text{-}O\\ |\\ CH_2\cdot N\end{matrix}\!\!\geqslant C\cdot NH_2,HBr$.

D. F. T.

Palladium. A. GUTBIER and C. FELLNER [with J. KRAÜTER, F. FALCO, A. KRELL, FR. SCHULZ, and M. WOERNLE] (*Zeitsch. anorg. Chem.*, 1916, **95**, 129—168. Compare A., 1905, i, 584, 876; 1906, i, 12, 244, 402; ii, 407; 1909, ii, 585; 1910, ii, 459, 756).—The following compounds are described: *tetramethylammonium palladochloride*, $(NMe_4)_2PdCl_4$, dark red, pleochroic crystals; iso*propylammonium palladochloride*, $(NH_3\cdot C_3H_7)_2PdCl_4$; n-*butylammonium palladochloride*, $(NH_3\cdot C_4H_9)_2PdCl_4$; *di*iso*butylammonium palladochloride*, $[NH_2(C_4H_9)_2]_2PdCl_4$; *allylammonium palladochloride*, $(NH_3\cdot C_3H_5)_2PdCl_4$; and the corresponding *mono-*, *di-*, and *tri-*iso*amylammonium*, *guanidinium*, *benzylanilinium*, o-, m-, and p-*chloro-* and *bromo-anilinium*, o-, m-, and p-*nitroanilinium*, *tribenzylammonium*, *dimethyl*-o-*toluidinium*, o-, m-, and p-*xylidinium*, *ψ-cumidinium*, 2 : 4-*tolylenediammonium*, *diphenylmethylammonium*, o- and p-*phenetidinium*, *β-picolinium*, *lutidinium*, *collidinium*, *piperidinium*, and iso*quinolinium palladochlorides*.

In the hexachloro-series, *dimethylammonium palladichloride*, $(NH_2Me_2)_2PdCl_6$ is bright red and unstable, and the *tri-* and *tetra-*

methylammonium, di-, tri-, and *tetra-ethylammonium,* iso*propylammonium, di-* and *tri-propylammonium,* n-*butylammonium, di-* and *tri-*iso*butylammonium, mono-, di-,* and *tri-*iso*amylammonium, β-picolinium, lutidinium, collidinium,* and iso*quinolinium palladichlorides* are quite similar.

The corresponding bromides of both series have been prepared from most of the same bases.

The following palladodiammine derivatives are described:

iso*Propylpalladosammine chloride,* $Pd(NH_2 \cdot C_3H_7)_2Cl_2$; and the corresponding *dipropyl,* n-*butyl, di-*iso*butyl, mono-,* and *di-*iso*amyl, benzylideneaniline,* o-, m-, and p-*nitroaniline,* o-, m-, and p-*xylidine,* 2:4- and 3:4-*tolylenediamine,* p-*phenetidine, β-picoline, lutidine, collidine, piperidine,* and iso*quinoline* compounds. Iodides and bromides of most of the bases have been prepared, as well as the *nitrates* from *pyridine,* $Pd(C_5NH_5)_2(NO_3)_2$, and *α-picoline,* $Pd(C_5NH_4Me)_2(NO_3)_2$. C. H. D.

A New Class of Palladium Compounds. Palladous Trichlorides and Tribromides. A. Gutbier and C. Fellner (*Zeitsch. anorg. Chem.*, 1916, **95**, 169—176).—Whilst palladous compounds with salts of organic amines usually correspond with two subsidiary valencies of the central atom, under certain conditions only one subsidiary valency may be active. This is very unusual, only one example being recorded in the large series of platinous compounds. The formation depends less on the relative proportions of the compounds than on the concentration, low concentrations favouring the trichloride and high concentrations the tetrachloride. Slow crystallisation at atmospheric temperatures is most suitable. The crystals are brown or red.

The *tripropylammonium,* $[NH(C_3H_7)_3]PdCl_3$, *di-* and *tri-*iso*butylammonium, guanidinium, aminoguanidinium,* and *benzylethylammonium chlorides,* and the *tetra-ethylammonium, tripropylammonium, collidinium,* and *tribenzylammonium bromides* are described. C. H. D.

Oxidation of Amino-acids and of Related Substances with Chloramine-T. Henry Drysdale Dakin (*Biochem. J.*, 1917, **11**, 79—95. Compare A., 1916, i, 598).—In a previous paper (*loc. cit.*) an account has been given of the oxidation of simple amino-acids by the neutral oxidising agent, chloramine-T (sodio-*p*-toluenesulphonchloroamide). The work has now been extended to a study of the behaviour of more complex amino-acids towards the same reagent.

When monosodium glutamate is treated with one molecular proportion of chloramine-T a good yield of the semi-aldehyde of succinic acid, β-aldehydopropionic acid, is obtained. The substance is readily isolated as the nitrophenylhydrazone, which crystallises in platelets, m. p. 185—187° (Alefeld, A., 1909, i, 364, gives 175°). Using two molecules of chloramine-T to one of the glutamate, the reaction takes a different course with formation of *β-cyanopropionic acid,* $C_4H_5O_2N$, crystallising in stout prisms, m. p. 48—50°. On

evaporation with concentrated hydrochloric acid, it is converted quantitatively into succinic acid, and by means of sodium and alcohol it is reduced to γ-aminobutyric acid. The latter substance has also been obtained by the bacterial decomposition of glutamic acid.

The oxidation of sodium aspartate by chloramine-T occurs readily in aqueous solution with the liberation of ammonia and carbon dioxide. The chief product isolated is dichloroacetaldehyde, which yields characteristic derivatives of glyoxal when treated with phenylhydrazine or *p*-nitrophenylhydrazine. Methylaspartic acid similarly yields derivatives of methylglyoxal with the intermediate formation of dichloroacetone, whilst *iso*butaldehyde and β-methylbutaldehyde are formed from valine and *iso*leucine respectively.

On oxidising aqueous solutions of asparagine with chloramine-T, a reducing substance is formed which on treatment with phenylhydrazine and other bases gives derivatives of mesoxalic semialdehyde. The substance is not isolated in the pure state, but the derivatives obtained from it indicate that it is probably the semialdehyde of dichloromalonamide, $CHO{\cdot}CCl_2{\cdot}CO{\cdot}NH_2$. Dichloroacetamide also occurs among the oxidation products of asparagine. On treating the oxidation products with phenylhydrazine, mesoxamide semialdehydebisphenylhydrazone,

$$CH(:N{\cdot}NHPh)C(:N{\cdot}NHPh){\cdot}CO{\cdot}NH_2,$$

is formed. It crystallises from ethyl acetate in light yellow prisms and needles, m. p. 250—252°. It is identical with a compound prepared by Langheld (A., 1909, i, 557), erroneously described by him as the phenylhydrazone of the amide of malonic semialdehyde. On boiling with dilute hydrochloric acid, it is converted into 4-benzeneazo-1-phenyl-5-pyrazolone. When *p*-bromophenylhydrazine is substituted for phenylhydrazine in the reaction, *mesoxamide semialdehydebis*-p-*bromophenylhydrazone*, $C_{15}H_{13}ON_3Br_2$, is formed. It crystallises in golden-yellow rosettes, m. p. 274—275°. The corresponding *bis*-p-*nitrophenylhydrazone*, $C_{15}H_{13}O_5N_7$, deep red, prismatic needles from nitrobenzene, m. p. about 340°, and *bis-semicarbazone*, $C_5H_9O_3N_7$, colourless needles, m. p. 240°, were also prepared. A trace of the nitrophenylhydrazone, when treated with sodium hydroxide and alcohol, gives an intense blue solution, a reaction which appears to be characteristic of two adjacent nitrophenylhydrazine groups. By treating the oxidation products of asparagine with 3:4-tolylenediamine, the *amide* of 7-methylquinoxaline-2(or 3)-carboxylic acid, $C_{10}H_9ON_3$, is formed, glistening plates, m. p. 286—287°.

On heating dextrose with chloramine-T in aqueous solution, oxidation occurs slowly and toluenesulphonamide is precipitated. The addition of phenylhydrazine to the filtrate is followed by the precipitation of a yellow substance, which is found to be the *phenylhydrazone* of *benzaldehyde*-p-*sulphonamide*, $C_{13}H_{13}O_2N_3S$, crystallising from alcohol in greenish-gold plates, m. p. 244—245° (decomp.). The aldehyde is produced apparently from *p*-toluenesulphonamide by oxidation with unchanged chloramine-T, and can also be prepared directly by heating these two substances together

in aqueous solution. On adding an alcoholic solution of aniline to the solution containing the aldehyde, *benzylideneaniline*-p-*sulphonamide*, $NH_2 \cdot SO_2 \cdot C_6H_4 \cdot CH{:}NPh$, is precipitated. It is obtained as a felted mass of silky crystals, m. p. 208°. On warming the anil with dilute sulphuric acid, the aldehyde is set free and can be extracted by ether. *Benzaldehyde*-p-*sulphonamide*, $C_7H_7O_3NS$, crystallises in shining, colourless plates and needles, m. p. 122—124°. It yields a *hydrazone*, $C_7H_9O_2N_3S$, shining plates, m. p. 288—290°, and a *semicarbazone*, $C_8H_{10}O_3N_4S$, characteristic twin prisms, m. p. 250—251°.

H. W. B.

The Origin of the Nitrogenous Pigments in Sugar Refinery Products. VL. STANĚK (*Zeitsch. Zukerind. Böhm.*, 1917, **41**, 607—614. Compare this vol., i, 381, and Stolzenberg, A., 1916, i, 829).—It has been suggested that the nitrogenous pigments (including "fuscazinic acid") in molasses and desaccharification residues may owe their formation to the condensation of amino-acids with sugars during the refinery processes. Maillard (A., 1912, i, 169) has already shown that many free amino-acids react with the common sugars to form such products, but the author has now tested whether such a condensation can take place in more or less alkaline solutions.

It is found that when solutions of invert-sugar or sucrose are heated in an autoclave at 105—130° with sodium glutamate or aspartate, or with asparagine, carbon dioxide is liberated, the solutions become acidic, and dark pigments are formed which are almost completely precipitated by lead acetate. The same pigments are obtained if precipitated chalk is added to overcome the acidity. Without the amino-acid, the colour of the solution is not so deep, and the pigment is completely soluble in alcohol. With the amino-acid, nitrogenous substances which do not dissolve in alcohol are produced as well. A fraction, which somewhat resembles fuscazinic acid in being a very dark brown powder, soluble only in alkalis, has been isolated. Asparagine and aspartic acid give rise to much more of this product than glutamic acid.

J. C. W.

The Nitrogenous Pigments of Molasses. H. FRIEDRICH (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 614—617).—The author claims that he has been engaged since 1914 on a method for the recovery of the various ingredients in molasses and on a study of the nitrogenous pigments. About 72% of the sucrose can be precipitated in a pure white condition by mixing the molasses with an equal quantity of cold glacial acetic acid. Most of this acid may be recovered in a concentration of 71% by distillation, when a dark brown, asphalt-like mass is left containing about 18% of ash (23·75% K). This residue may be worked up for betaine by trituration with about six times its bulk of methyl alcohol. The insoluble portion (27%) is a nitrogenous pigment containing about 3·4% of nitrogen, and yielding yellow derivatives on nitration.

The author agrees with Staněk (see preceding abstract) as to

the nature of the nitrogenous pigment, except that he regards the condensation of the amino-acids as taking place with caramel substances rather than with the sugars themselves. He therefore proposes the term "caramelazine substances." J. C. W.

The Nitrogenous Pigments of Molasses. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 618).—A reply to Friedrich (preceding abstract). He points out that the pigments which he has obtained by heating solutions of sugars and salts of amino-acids were formed at temperatures below that at which caramel is produced. He also suggests that Friedrich is dealing, not only with the original pigments of molasses, but also with new ones produced during the distillation by the condensation of the invert-sugar and amino-acids under the influence of the acetic acid.
J. C. W.

Condensation Product of Ammonium Thiocyanate with Formaldehyde. SCHMERDA (*Zeitsch. angew. Chem.*, 1917, **30**, i, 176).—In concentrated aqueous solution, ammonium thiocyanate combines directly with formaldehyde; 1 mol. or more of formaldehyde unites with 1 mol. of thiocyanate. The product is only sparingly soluble in water or ordinary solvents, and is decomposed by strong acids or alkalis. W. P. S.

Salts of Thiocarbamide. AUGUSTUS EDWARD DIXON (T., 1917, **111**, 684—690).—Since the solubility of thiocarbamide in water is increased by the presence of strong acids, it appears that salts are formed in these solutions, but these are markedly hydrolysed and their isolation is difficult. The hydrochloride (Stevens, T., 1902, **81**, 80) is now found to dissolve to the extent of 1·48 parts to 6·65 parts of water. It has the formula CH_4N_2S,HCl, m. p. 136—137°. A salt with 2HCl was not detected. With sulphuric acid, the salt isolated has the formula CH_4N_2S,H_2SO_4, and is a white, crystalline, hygroscopic substance. The nitrate (Emerson Reynolds, this Journ., 1869, **22**, 5) is soluble, for 1 part of thiocarbamide, in about 6·5 parts of water. The oxalate, $CH_4N_2S,H_2C_2O_4$, melts at 73—74°. The trichloroacetate,

$$CH_4N_2S,C_2HO_2Cl_3,$$

and the picrate, $CH_4N_2S,C_6H_3O_7N_3$, were also prepared. The constitution of these salts is briefly discussed. T. S. PA.

Amides and Imides of Tartaric Acid. I. L. CASALE (*Gazzetta*, 1917, **47**, i, 272—285).—*d*-Tartaric acid forms with aniline two salts, namely, aniline hydrogen *d*-tartrate and aniline *d*-tartrate, $[\cdot CH(OH)\cdot CO_2H,NH_2Ph]_2+4H_2O$ (Hilditch, T., 1911, **99**, 224, gave $3H_2O$), which lose water of constitution when heated, yielding the corresponding imide and amide respectively. Phenyltartrimide readily takes up: (1) 1 mol. of water, to form an amic acid; (2) 1 mol. of alcohol, to form an ester of such amic acid; and (3) 1 mol. of ammonia or of an amine, to form a diamide. The chemical behaviour of phenyltartrimide pointed to a lactidic

constitution, but such a conclusion is excluded by the results of a molecular weight determination in acetone.

d-Phenyltartrimide (tartranil) forms nacreous leaflets with straw-coloured reflection, m. p. 255° (corr.; decomp.). Its solubility in cold water is very slight, and cannot be determined owing to the transformation of the compound into tartranilic acid. The value given by Frankland and Slator (T., 1903, **83**, 1349) for the specific rotation of *d*-phenyltartrimide in an aqueous solution containing 0·5964 gram per 100 grams of the solvent is invalid, such concentration being unattainable with the pure compound; it has the normal molecular weight in boiling acetone, and its specific rotation in methyl alcohol is $[\alpha]_D^{15}$ +130°.

d-*Phenyltartramic* (*tartranilic*) *acid*,

$$NHPh\cdot CO\cdot [CH(OH)]_2\cdot CO_2H,$$

forms white, silky needles, m. p. 194° (corr.), and behaves as a weak monobasic acid; in aqueous solution, the value of $[\alpha]_D^{15}$ is +105·6—106·8°, and in methyl alcohol, +114·7°. When heated, the acid yields tartranil, m. p. 255° (corr.), and an isomeride of the latter, m. p. 262° (corr.). The following salts of tartranilic acid were prepared: *sodium*, m. p. 226° (corr.), $[\alpha]_D^{15}$ +101·25°; *ammonium*, $[\alpha]^1{}_D$ +102·2°; *silver*; *methyl*, colourless needles, m. p. 175° (corr.), $[\alpha]_D^{15}$ +106°; *ethyl*, prismatic needles, m. p. 163° (corr.), $[\alpha]_D^{15}$ +102·4°; *propyl*, m. p. 161° (corr.), $[\alpha]_D^{15}$ +99·1°; iso*butyl*, m. p. 158° (corr.), $[\alpha]_D^{15}$ +92·6°; iso*amyl*, m. p. 139° (corr.), $[\alpha]_D^{15}$ +89·2°.

d-*Monophenyltartramide* (*tartranilamide*),

$$NHPh\cdot CO\cdot [CH\cdot OH]_2\cdot CO\cdot NH_2,$$

prepared by dissolving phenyltartrimide in hot concentrated ammonia solution, forms shining, white leaflets, m. p. 226° (corr.), $[\alpha]_D^{15}$ +139° in water or +153° in methyl alcohol. T. H. P.

Action of Sodium Hypochlorite on Amides of α-Hydroxy-acids and of Polyhydroxy-acids having a Hydroxyl Group in the α-Position. A New Method for the Degradation of Sugars. R. A. Weerman (*Rec. trav. chim.*, 1917, **37**, 16—51).—A more detailed account and an extension of work already published (compare A., 1915, i, 387). Among the products of the addition of hydrazine sulphate to a mixture of mandelamide and sodium hypochlorite in methyl alcohol, azodicarbonamide was given instead of hydrazodicarbonamide.

By the method described (*loc. cit.*), *l*-mannose was converted through *l*-mannonamide into *l*-arabinose, and *l*-arabinose through l-*arabonamide*, m. p. 132—133° (decomp.), $[\alpha]_D^{14}$ +38·4°, into *l*-erythrose, isolated as its phenylbenzylhydrazone. Attempts to carry out the degradation of *l*-gulose, *l*-ribose, *l*-xylose, *iso*saccharinamide, and phenylglyceramide were not successful, owing to the instability or the poor yields of the necessary amides.

The author has obtained tartramic acid in a crystalline form, m. p. 171—172°, $[\alpha]_D^{13}$ +63·7°, and the crystallographic measurements confirm those of Pasteur (*Ann. Chim. Phys.*, 1853, [iii], **38**, **454**).

The action of sodium hypochlorite on the amides of hydroxy-acids furnishes a ready means of showing whether there is a hydroxyl group in the α-position. If to the reaction mixture semicarbazide is added and hydrazodicarbonamide is formed, the presence of a hydroxyl group in the α-position is indicated. W. G.

Imino-esters. III. The Constitution of Salts of the Imino-esters. ANGELO KNORR (*Ber.*, 1917, **50**, 767—772).—The conversion of the esters of thioncarbamic acid, $NH_2\cdot CS\cdot OR$, into the corresponding thiolcarbamates, $NH_2\cdot CO\cdot SR$, under the influence of alkyl haloids, has been attributed to the intermediate formation of an additive compound of the thioncarbamate and the alkyl haloid, the subsequent re-elimination of the haloid giving rise to the thiolcarbamate (Wheeler and Barnes, A., 1899, i, 797). The author has now found that an additive compound of this type actually is formed in the action of methyl iodide on ethyl thioncarbamate (xanthogenamide), but that the constitution of this product is that of a *hydriodide* of *ethyl iminomethylthiolcarbonate*, SMe·C(OEt):NH,HI; this forms needles, m. p. 58—60°, decomposing into ethyl iodide and methyl thiolcarbamate, $NH_2\cdot CO\cdot SMe$; its constitution was further demonstrated by conversion into the corresponding hydrochloride by successive treatment with potassium carbonate solution and ethereal hydrogen chloride and also into the *acetyl* derivative, SMe·CO·NHAc, prisms, m. p. 144°, by the action of acetic anhydride; the analogous *acetyl* derivative of ethyl thiolcarbamate, SEt·CO·NHAc, prisms, m. p. 97—98°, was obtained by the action of acetic anhydride on ethyl iminoethylthiolcarbonate or on the hydrochloride of this compound.

For the explanation of this transformation the author suggests the stages $NH_2\cdot CS\cdot OEt + MeI \longrightarrow NH_2\cdot CI(SMe)\cdot OEt \longrightarrow$
SMe·C(OEt):NH,HI,
the intermediate carbonium salt occurring only transiently (compare Wheeler and Barnes, *loc. cit.*; Biilmann, A., 1909, i, 143). The results of the investigation confirm Pinner's views as to the constitution of the salts of the imino-esters. D. F. T.

Crystallography of some Compounds of Glutamic Acid and Glutiminic Acid. L. KAPLANOVA (*Abh. Bhöm Akad.*, 1915, No. 23, 8 pp.; from *Jahrb. Min.*, 1917, i, 123—124).—An interesting example of pseudoracemism and racemism with morphotropy is given by the following group of salts of glutamic acid:

	Active.	Inactive.
Hydrochloride......	Rhombic, 0·8852 : 1 : 0·3866 D 1·525	Ditto D 1·525
Hydrobromide......	Rhombic, 0·8784 : 1 : 0·4033 D 1·790	Ditto D 1·814
Hydriodide	Rhombic, 0·8835 : 1 : 0·4318 D 1·982	Triclinic D 2·030

The interfacial angles of the triclinic inactive hydriodide approach the corresponding angles of the active rhombic crystals. The

optical orientation and cleavage are identical in the hydrochlorides and hydrobromides, but differ somewhat in the hydriodides.

L. J. S.

Electrolytic Diazotisation of an Aliphatic Compound. Robert B. Krauss (*J. Amer. Chem. Soc.*, 1917, **39**, 1427—1431).—When a current of 3·5 amperes at 7 volts is run for about four hours through a cell comprising a copper cooling coil as cathode in 30% sodium hydroxide, and a rotating platinum gauze anode in a solution of glutamic acid (30), sodium nitrite (30), and sodium hydroxide (34), there is every indication of the production of the *iso*-diazotate. The anolyte becomes orange-yellow, and from it a creamy solid may be isolated, which yields a *p*-chlorobenzoyl derivative, m. p. 191°, and a β-naphthalenesulphonyl compound, m. p. 185—186°, and gives typical dyes on coupling with aromatic bases. It is hoped that the compound may soon be obtained pure enough for a thorough characterisation.

J. C. W.

The Hydrazides of Acids Produced by the Oxidation of Sugars. R. A. Weerman (*Rec. trav. chim.*, 1917, **37**, 52—66).—In an endeavour to find a method for the degradation of sugars without the accompanying formation of metallic salts, the hydrazides of the acids arising from the oxidation of certain sugars have been prepared, but are not suitable for the object in view. These hydrazides readily give condensation products with benzaldehyde.

d-Gluconolactone when boiled in alcoholic solution with hydrazine hydrate gives d-*gluconic hydrazide*, m. p. 142—144° (decomp.), $[\alpha]_D^{16}$ +30·6°, which with nitrous acid gives s-*digluconic hydrazide*, $C_{12}H_{24}O_{12}N_2,H_2O$, m. p. 178—179°, $[\alpha]_D^{19}$ +66·4°, and with benzaldehyde gives d-*gluconic benzylidenehydrazide*,

$$C_5H_{11}O_5\cdot CO\cdot NH\cdot N\colon CHPh,$$

m. p. 157—158°. l-*Mannonic hydrazide*, m. p. 161—162°, $[\alpha]_D^{14}$ +4·4°, gives a *benzylidenehydrazide*, m. p. 194—195°. l-*Arabonic hydrazide* has m. p. 138—139°, $[\alpha]_D^{15}$ +51·9°. m-*Saccharinic hydrazide*,

$$HO\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CO\cdot NH\cdot NH_2,$$

m. p. 122—123°, $[\alpha]_D^{11}$ +18·1°, behaves somewhat differently from the other hydrazides in that carbon dioxide is among the products of its decomposition with nitrous acid.

W. G.

The Crystalline Form of Diphenyliodonium Chloride, $C_{12}H_{10}ICl$. A. L. W. E. van der Veen (*Zeitsch. Kryst. Min.*, 1916, **55**, 372—373).—The crystals are monoclinic sphenoidal [$a:b:c$ = 1·2195 : 1 : 1·1871; β = 102°15′]. They were grown from aqueous solution, and it is noteworthy that all were of the left-handed type, no crystals of the enantiomorphous type being obtained. Cleavage on {100} perfect. The optic axial plane is {010}. D 1·67 ± 0·005.

E. H. R.

Crystallographic Investigation of some Nitro-derivatives of Benzene. H. Steinmetz (*Zeitsch. Kryst. Min.*, 1915, **54**, 467—497).—*m*-Dinitrobenzene forms rhombic, bipyramidal crystals

[$a:b:c=0.9435:1:0.5434$]; cleavage {100}; D 1·570; M.V. 107·01.

o-Chloronitrobenzene and *o*-bromonitrobenzene crystallise in the monoclinic system, whilst *o*-iodonitrobenzene is rhombic. Owing to paucity of forms developed, neither could be measured completely.

m-Chloronitrobenzene crystallises in the pyramidal class of the rhombic system, the crystals being markedly hemimorphic [$a:b:c=0.5604:1:0.5004$]. Cleavage {010} perfect; {100} poor. D^{15} 1·582; M.V. 99·56.

m-Bromonitrobenzene is isomorphous with the last [$a:b:c=0.5490:1:0.4928$]; D 1·969; M.V. 102·59.

m-Iodonitrobenzene forms monoclinic crystals [$a:b:c=2.2920:1:2.2581$; $\beta=104°14'$]. It is, however, pseudorhombic, and when the axial ratios are put into the rhombic form, a close, morphotropic relationship to the two preceding compounds becomes apparent. Cleavage {100} perfect, {001} poor; D 2·227; M.V. 111·81.

p-Chloronitrobenzene is monoclinic [$a:b:c=1.9661:1:1.1265$; $\beta=97°21'$]. Cleavage poor, {100} and {110}. D 1·520; M.V. 103·62.

p-Bromo- and *p*-iodo-nitrobenzene are isomorphous, forming triclinic crystals. There is little evidence of isodimorphism with the *p*-chloro-compound.

The three following compounds are closely isomorphous:

3:5-Dichloro-1-nitrobenzene, monoclinic [$a:b:c=0.6017:1:0.2847$; $\beta=121°20'$]; cleavage {010} perfect; {100} and {001} poor; D 1·712; M.V. 112·15.

3-Chloro-5-bromo-1-nitrobenzene [$a:b:c=0.5902:1:0.2850$; $\beta=122°37'$]; D 2·048; M.V. 115·48.

3:5-Dibromo-1-nitrobenzene [$a:b:c=0.5795:1:0.2839$; $\beta=123°48'$]; D 2·363; M.V. = 118·91.

o-Nitrophenol forms monoclinic crystals [$a:b:c=0.8932:1:0.4769$; $\beta=103°34'$]. Cleavage {010}. D 1·495; M.V. 92·98.

m-Nitrophenol, monoclinic [$a:b:c=0.9223:1:0.15(26)$; $\beta=120°21'$]. Cleavage {110} perfect, {120} less perfect. D 1·492; M.V. 93·16.

2:6-Dinitrophenol is rhombic bipyramidal [$a:b:c=0.9510:1:0.7449$]. The density of the crystals varied between 1·645 and 1·724. The latter value gives M.V. 111·86.

3:4-Dinitrophenol forms triclinic crystals, D 1·672; M.V. 110·05.

2:3-Dinitrophenol, monoclinic [$a:b:c=1.6133:1:0.9525$; $\beta=111°27\frac{1}{2}'$]; D 1·681; M.V. 109·46. Cleavage {001}.

3:5-*Dinitrophenol*, monoclinic [$a:b:c=0.6816:1:0.3313$; $\beta=100°4'$]; cleavage {001}; D^{20} 1·702; M.V. 108·11. E. H. R.

The Crystalline Form of some Benzene Derivatives. E. Repossi (*Rend. R. Ist. Lomb. sci. lett.*, 1912, (ii[a]), **45**, 242—271; from *Zeitsch. Kryst. Min.*, 1915, **55**, 281—288).—The author has examined the crystalline form of ten of the possible

3 : 4 : 5-trihalogen derivatives of nitrobenzene. The six possible compounds containing chlorine and bromine form an isomorphous triclinic series. In addition, 3 : 5-dichloro-4-bromonitrobenzene exists in a β-monoclinic modification, which is structurally similar to, though not truly isomorphous with, the monoclinic series of compounds containing iodine, of which four have been examined.

3 : 4 : 5-Trichloro-1-nitrobenzene, triclinic, tabular crystals from ethyl acetate, m. p. 72·5° [$a:b:c=1·1855:1:0·4420$; $\alpha=103°11\frac{1}{2}'$; $\beta=91°23'$; $\gamma=77°32'$]. D 1·807; M.V. 125·3. The axial ratios of the other triclinic compounds are similar.

3 : 4-Dichloro-5-bromo-1-nitrobenzene, bright greenish-yellow, triclinic crystals from a mixture of alcohol and ether; m. p. 82·4°. D 2·074; M.V. 130·63.

3 : 5-Dichloro-4-bromo-1-nitrobenzene, tabular, sulphur-yellow, triclinic (α-modification) crystals from ethyl acetate; m. p. 88°. D 2·077; M.V. 130·44.

The β-modification forms monoclinic prisms or tables from ethyl acetate or a mixture of this with alcohol and benzene [$a:b:c=0·9227:1:1·0166$; $\beta=92°14'$]. D 2·079; M.V. 130·3. The crystals become cloudy after a time.

5-Chloro-3 : 4-dibromo-1-nitrobenzene, greenish-yellow, triclinic tables from a mixture of alcohol and ether; m. p. 97·2°. D 2·376; M.V. 132·75.

4-Chloro-3 : 5-dibromo-1-nitrobenzene, bright greenish-yellow, triclinic crystals, rich in faces, from mixed solvents, such as benzene, alcohol, and ethyl acetate; m. p. 92°. D 2·397; M.V. 131·59.

3 : 4 : 5-Tribromo-1-nitrobenzene, bright yellow, prismatic, triclinic crystals from the usual solvents; m. p. 112°. D 2·645; M.V. 138·37.

3 : 4 : 5-Tri-iodo-1-nitrobenzene, sulphur-yellow, monoclinic prisms from chloroform, m. p. 167° [$a:b:c=0·8276:1:0·9646$; $\beta=90°5'$]. The crystals are plastic at the ordinary temperature and under slight pressure form twins, $\{\bar{1}02\}$ being a gliding plane and also a cleavage plane. D 3·265; M.V. 133·35.

5-Chloro-3 : 4-di-iodo-1-nitrobenzene, orange-yellow crystals, monoclinic prisms, from chloroform; m. p. 146·5° [$a:b:c=0·9143:1:0·9936$; $\beta=92°4'$].

4-Chloro-3 : 5-di-iodo-1-nitrobenzene, monoclinic prisms from ethyl acetate; m. p. 110° [$a:b:c=0·8137:1:0·9748$; $\beta=90°38'$]. D 2·827; M.V. 144·75.

5-Bromo-3 : 4-di-iodo-1-nitrobenzene, imperfect, sulphur-yellow, monoclinic prisms from chloroform; m. p. 146·5° [$a:b:c=0·8184:1:0·9350$; $\beta=91°34'$]. D 3·085; M.V. 147·1. E. H. R.

Some Derivatives of Benzenesulphinic Acid. S. C. J. Olivier (*Rec. trav. chim.*, 1917, **37**, 92—95).—The compound $C_6H_4Br·SO_2·AlBr_2$, obtained by the action of aluminium bromide on *p*-bromobenzenesulphonyl bromide in solution in carbon disulphide, behaves like aluminium bromide in that it will give additive compounds with certain aromatic sulphones.

If diphenylsulphone is dissolved in dry benzene and aluminium

bromide is added, a clear solution results, from which on the addition of *p*-bromobenzenesulphonyl bromide a viscous liquid separates out, which is the *compound* $C_6H_4Br \cdot SO_2 \cdot AlBr_2,SO_2Ph_2$. When this compound is decomposed by water, *p*-bromobenzenesulphinic acid and the sulphone are obtained. Three other such *compounds* were similarly prepared having the following compositions:

$$C_6H_4Br \cdot SO_2 \cdot AlBr_2,C_6H_4Br \cdot SO_2Ph,$$
$$C_6H_4Br \cdot SO_2 \cdot AlBr_2,C_6H_4I \cdot SO_2Ph,$$

and $C_6H_4Br \cdot SO_2 \cdot AlBr_2,C_6H_4Me \cdot SO_2Ph$. All these compounds had properties similar to those of the first. W. G.

Triphenylmethyl. XXVII. Molecular Weights of the Triarylmethyls. M. GOMBERG and C. S. SCHOEPFLE (*J. Amer. Chem. Soc.*, 1917, **39**, 1652—1674).—Triphenylmethyl, diphenyl-α-naphthylmethyl, phenylxanthyl, *p*-tolylxanthyl, *p*-chlorophenylxanthyl, α-naphthylxanthyl, and phenylpheno-β-naphthaxanthyl have been prepared in a pure condition and their molecular weights determined in freezing naphthalene over a fairly wide range of concentration. Under the conditions used, diphenyl-α-naphthylmethyl and α-naphthylxanthyl are entirely unimolecular.

In all cases, the molecular weight increases gradually as the concentration increases from 1% to 6%, molecular dissociation being thus indicated. When in triphenylmethyl two phenyl groups become joined through an oxygen atom, and thus give rise to a xanthone ring, the tendency to dissociate is markedly increased. A phenyl and a *p*-tolyl group are apparently equivalent in their influence for dissociation when linked to a xanthone ring, whereas the influence of a *p*-chlorophenyl group is somewhat less. An α-naphthyl group when replacing a phenyl group in triphenylmethyl exerts on the dissociation equilibrium of the compound a decided influence in favour of the unimolecular phase, diphenyl-α-naphthylmethyl being wholly dissociated. This influence is retained when the naphthyl group is linked to a xanthone ring, the resulting compound being also completely dissociated. When, however, the naphthyl group enters as a component in the formation of the xanthone ring itself, it causes a considerable lowering of the tendency of the compound to dissociate.

The triarylmethyls are almost wholly devoid of colour in the solid state, whereas their solutions are yellow, orange, brown, red, or green, the coloration being regarded as due to tautomerisation of the compounds into their quinonoid modifications. T. H. P.

1 : 2- and 2 : 3-Diphenylindene. PAUL RUGGLI (*Annalen*, 1917, **414**, 125—130).—By the addition of bromine to αβγ-triphenylpropene, and subsequent elimination of hydrogen bromide, Orechoff (A., 1914, i, 265) obtained a hydrocarbon, m. p. 178°, which he designated 2:3-diphenylindene. A compound, m. p. 108°, which must have this constitution, was previously obtained from benzylidenedeoxybenzoin by Thiele and Ruggli (A., 1912,

i, 866). It is now shown that Orechoff's compound was the other alternative of his reaction, namely, 1:2-*diphenylindene*,

$$C_6H_4<\begin{matrix}\text{---}CH\\ CHPh\end{matrix}>CPh.$$

Orechoff's objection to this formula was that the hydrocarbon condensed with benzaldehyde to form 2:3-diphenyl-1-benzylideneindene, but this is explained by the fact that 1:2-diphenylindene undergoes rearrangement into the 2:3-compound, which yields the same condensation product, in the presence of potassium hydroxide. J. C. W.

I-Phenanthrene-10:3 (or 6)-disulphonic Acid. HÅKAN SANDQVIST (*Ber.*, 1917, **50**, 774—777).—The author provisionally distinguishes between the two isomeric 10-bromophenanthrene-3- or -6-sulphonic acids (A., 1915, i, 795; 1916, i, 206; ii, 556) by the prefixes I and II. The I-isomeride slowly reacts with aqueous sodium sulphite solution at 260—270°, with the formation of the easily soluble *sodium* salt (needles) of I-*phenanthrene*-10:3(or 6)-*disulphonic acid*, $C_{14}H_8(SO_3H)_2,4H_2O$, needles, m. p. 157° with rapid heating, or when anhydrous, m. p. 233° (decomp.); *barium* salt, rhombic crystals with $2\frac{1}{2}H_2O$. The corresponding acid *chloride*, $C_{14}H_8O_4Cl_2S_2$, prepared by the action of phosphorus pentachloride on the sodium salt, forms yellow prisms, which melt at 220—221° with liberation of sulphur dioxide and a little hydrogen chloride, and with the formation of a substance, m. p. 196—197°, probably I-10-chlorophenanthrene-3(or 6)-sulphonic acid.

The disulphonic acid does not resemble the I-10-bromo-3(or 6)-sulphonic acid in the characteristic behaviour of the aqueous solutions of the latter with respect to viscosity and anisotropy. D. F. T.

Methods for the Acylation of Aromatic Amino-compounds and Carbamides, with especial Reference to Chloroacetylation. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1439—1447).—Chloroacetyl-, benzoyl-, and α-chlorophenylacetyl derivatives of amines are very conveniently prepared by adding a slight excess of the acyl chloride to a chilled solution of the base in a mixture of equal parts of glacial acetic acid and concentrated sodium acetate solution. The products usually crystallise out as formed. Chloroacetylation of carbamides is best performed by dissolving or suspending the compounds in molten chloroacetic acid and then adding the chloride.

The following compounds have been prepared by these methods. α-Chloroacetanilide, m. p. 136—137°; *chloroaceto*-p-*iodoanilide*, $C_6H_4I{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, m. p. 191—194°; *m*-chloroacetylaminophenol (A., 1915, i, 671); p-*chloroacetylaminophenol*, rosettes of glistening platelets, m. p. 144·5—146° (corr.); o-*chloroacetylaminobenzamide*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, silky hairs, m. p. 183—184·5°; m-*chloroacetylaminobenzamide*, aggregates of minute crystals, m. p. 215°, which forms a *hexamethylenetetraminium* salt, $C_{15}H_{21}O_2N_6Cl$,

m. p. 169—170° (decomp.); m-*chloroacetylaminobenzoic acid*, m. p. 230—232° (decomp.); p-*chloroacetylaminobenzamide*, silky needles, m. p. 241—243° (decomp.); *p*-aminophenylacetamide, scales, m. p. 161—162° (corr.); p-*chloroacetylaminophenylacetamide*, thin, rectangular plates, m. p. 191—191·5° (corr.).

p-α-*Chlorophenylacetylaminophenylcarbamide*,

$$CHPhCl\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2,$$

crystallises in minute platelets and needles, m. p. 200—201° (decomp.); m-α-*chlorophenylacetylaminophenol*, forms aggregates of spindles, m. p. 157—158° (decomp.); m-α-*chlorophenylacetylaminobenzamide*, separates in minute platelets, m. p. 218° (decomp.); p-α-*chlorophenylacetylaminophenylacetamide*,

$$CHPhCl\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2,$$

forms thin plates and needles, m. p. 184·5—185·5°.

o-Carbamidophenol is benzoylated in pyridine solution and the product, o-*carbamidophenyl benzoate*, aggregates of minute spears, m. p. 178—179° (corr.), converted by the method indicated above into o-*chloroacetylcarbamidophenyl benzoate*,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot OBz,$$

voluminous rosettes of silky hairs, m. p. 219° (decomp.). Similarly, m-*carbamidophenyl benzoate*, lenticular plates, m. p. 183—184° (corr.), yields m-*chloroacetylcarbamidophenyl benzoate*, in rosettes of long, flat needles, m. p. 188—189·5°. J. C. W.

The Crystalline Form of some Benzene Derivatives. E. Artini (*Rend. R. Ist. Lomb. sci. lett.*, 1912, (ii), **45**, 632—644; from *Zeitsch. Kryst. Min.*, 1915, **55**, 288—291).—Crystals of the six possible 2:6-dihalogen derivatives of *p*-nitrodiacetanilide have been examined. The dichloro-, chlorobromo-, and chloroiodo-compounds form a monoclinic isomorphous series, whilst the dibromo-compound is symmorphous with these, but is triclinic. The bromoiodo- and di-iodo-compounds form a distinct triclinic group.

2:6-Dichloro-4-nitrodiacetanilide [$a:b:c=1·1361:1:0·8753$; $\beta=70°4'$]. M. p. 142—143°. D 1·565; M.V. 185·98.

2-Chloro-6-bromo-4-nitrodiacetanilide [$a:b:c=1·1127:1:0·8509$; $\beta=70°36'$]. M. p. 139°. D 1·749; M.V. 191·86.

2-Chloro-6-iodo-4-nitrodiacetanilide [$a:b:c=1·038:1:0·799$; $\beta=108°16'$]. M. p. 113°. D 1·913; M.V. 199·93.

2:6-Dibromo-4-nitrodiacetanilide [$a:b:c=1·0901:1:0·8325$; $\alpha=88°43'$; $\beta=109°10'$; $\gamma=86°34'$]. D 1·939; M.V. 196·02.

2-Bromo-6-iodo-4-nitrodiacetanilide [$a:b:c=0·9470:1:0·7288$; $\alpha=96°1'$; $\beta=102°33'$; $\gamma=80°53'$]. M. p. 134°; D 2·112; M.V. 202·16.

2:6-Di-iodo-4-nitrodiacetanilide [$a:b:c=0·9682:1:0·7260$; $\alpha=83°7'$; $\beta=76°8\frac{1}{2}'$; $\gamma=99°43'$]. M. p. 170—171°; D 2·290; M.V. 206·93. E. H. R.

The Different Methods of Decomposition of Amines by Catalysis: Regeneration of Aniline from Substituted Anilines. Paul Sabatier and G. Gaudion (*Compt. rend.*, 1917, **165**, 309—313).—When the vapour of methylaniline is passed over

reduced nickel at 350°, there is an evolution of ammonia and methane, but the principal product is aniline. The first reaction is $NHPhMe = NH_2Ph + CH_2$. The methylene groups are decomposed into carbon and hydrogen, which then gives rise to the reaction $NHPhMe + 2H_2 = C_6H_6 + NH_3 + CH_4$. This reaction is, however, of minor importance, the principal change being $2NHMePh = C + CH_4 + 2NH_2Ph$. Dimethylaniline similarly gives aniline, carbon, and methane. Ethylaniline is decomposed according to the equation $NHEtPh = NH_2Ph + C_2H_4$. The ethylene is immediately decomposed by the nickel, giving carbon and a mixture of methane, ethane, and hydrogen. Diethylaniline behaves similarly. W. G.

Trinitrophenylmethylnitramine (Tetranitromethylaniline). C. F. van Duin (*Rec. trav. chim.*, 1917, **37**, 111—117).—For the safe preparation of trinitrophenylmethylnitroamine in quantity and in order to obtain a good yield, the author considers it necessary to modify Langenscheidt's process (compare A., 1913, i, 457). One hundred grams of dimethylaniline are dissolved in 1 kilogram of sulphuric acid, the temperature being kept below 25°. This solution is poured drop by drop into 500 c.c. of nitric acid (D 1·49), the temperature being kept between 38° and 42° during this process and for three hours after. The temperature is then slowly raised to 50° for half an hour and finally to 55° for two hours. The mixture is allowed to cool and the next day is filtered on glass-wool and washed free from acid with water and then once with alcohol. The substance thus prepared is very stable. It is only very slowly decomposed when boiled with water, giving picric acid.

[With B. C. Roeters van Lennep.]—The authors consider that the temperature given by Flürscheim and Simon (P., 1910, **26**, 81) for the preparation of tetranitroaniline is too high, and that the temperature during this process should not exceed 50°, the mixture being allowed to remain one day between two heatings for two hours at 50°. After two months, tetranitroaniline commences to decompose, nitrous acid being evolved. W. G.

Some 2:6-Dinitrobenzyl Derivatives. S. Reich and A. Oganessian (*Bull. Soc. chim.*, 1917, [iv], **21**, 117—120).—2:6-Dinitrotoluene is best brominated in the side-chain by heating it in a sealed tube with bromine and magnesium carbonate (compare Rheinhold, "Thesis," Grenoble, 1914). The 2:6-dinitrobenzyl bromide thus obtained gives, with potassium iodide, 2:6-*dinitrobenzyl iodide*, m. p. 100—101°. With a concentrated aqueous solution of potassium cyanide an alcoholic solution of the bromide gives 2:6-*dinitrophenylacetonitrile*, yellowish-brown crystals, m. p. 202°. If a benzene solution of 2:6-dinitrobenzyl bromide is saturated with ammonia, 2:6:2′:6′-*tetranitrodibenzylamine*, pale yellow needles, m. p. 194°, is obtained, giving a *sulphate*, m. p. 235°; a *hydrobromide*, m. p. 202°; a *platinichloride*, m. p. 236°; a *nitrosoamine*, m. p. 173°; and an *acetyl* derivative, m. p. 189°. When a molecular mixture of dinitrobenzyl bromide and potassium phthalimide is heated for three hours at 130—135° it yields 2:6-*dinitrobenzyl-*

phthalimide, m. p. 178°, which, when heated with fuming hydrochloric acid in a sealed tube at 170—180° for six hours, yields 2:6-*dinitrobenzylamine*, brown needles, m. p. 88°, giving a *hydrochloride*, m. p. 185°, and a *platinichloride*, m. p. 193°. W. G.

A Series of Four Primary Amines, having the Amino group Linked to a Tertiary Carbon Atom, and some of their Derivatives. M. BRANDER (*Rec. trav. chim.*, 1917, **37**, 67—87).—The four amines, *tert.*-butylamine, α-phenyl*iso*propylamine, αα-diphenylethylamine, and triphenylmethylamine, have been prepared, and their behaviour towards certain reagents studied. They can all be prepared by the action of ammonia on the corresponding alkyl chloride. The first amine was only obtained in very small amount, but a much larger yield of the second was obtained. *αα-Diphenylethylamine*, $CMePh_2{\cdot}NH_2$, is a colourless, odourless liquid, b. p. 161—162°/13 mm.

Triphenylmethylamine hydrochloride is readily decomposed by water at 100°, giving triphenylmethylcarbinol. With αα-diphenylethylamine hydrochloride the decomposition is very slow at 100°, but it proceeds much more rapidly at 200°, a considerable quantity of the unsaturated hydrocarbon being formed. With *tert.*-butylamine hydrochloride the decomposition is still more difficult, no change occurring at 160°, but the unsaturated hydrocarbon is formed at 280° after fourteen hours.

With triphenylmethyl chloride in benzene solution, *tert.*-butylamine gives *triphenylmethyl*tert.*-butylamine*, $CPh_3{\cdot}NH{\cdot}CMe_3$, m. p. 94·5°. A change occurred when this alkyl chloride was heated in benzene solution with phenyl*iso*propylamine, but no product could be isolated.

With silver nitrate the hydrochlorides of these amines give the corresponding nitrites. tert.*-Butylamine nitrite* has m. p. 126—127° (decomp.), *phenyl*iso*propylamine nitrite* has m. p. 98—99° (decomp.), *αα-diphenylethylamine nitrite* has m. p. 96—97° (decomp.), and *triphenylmethylamine nitrite* has m. p. 120° (decomp.) when heated quickly.

With benzoyl chloride in dry ethereal solution the four amines gave benzoyl derivatives. *Benzo*tert.*-butylamide*, $NHBz{\cdot}CMe_3$, slender needles, has m. p. 136·5°; *benzo-α-phenyl*iso*propylamide*, m. p. 159°; *benzo-αα-diphenylethylamide*, m. p. 150·5° (decomp.), and *benzotriphenylmethylamide*, m. p. 165·5°. The amines also react with oxalyl chloride, giving the corresponding oxamides. *Di-*tert.*-butyloxamide*, $(CMe_3{\cdot}NH{\cdot}CO)_2$, has m. p. 176°; *di-α-phenyl*iso*propyloxamide*, needles, m. p. 131°; *di-αα-diphenylethyloxamide*, m. p. 228°; and *ditriphenylmethyloxamide*, m. p. 349°. These same oxamides were obtained by the action of ethyl oxalate on the amine, but in this reaction αα-diphenylethylamine gave, in addition, *ethyl αα-diphenylethyloxamate*, m. p. 134°, which with liquid ammonia yielded *αα-diphenylethyloxamide*, $CMePh_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, m. p. 145°, and triphenylmethylamine gave some *ethyl triphenylmethyloxamate*, m. p. 155° (decomp.).

When warmed with potassium cyanate in aqueous solution the

hydrochlorides of the four amines yield the corresponding carbamides, the yield diminishing rapidly in passing up the series from *tert.*-butylamine to triphenylmethylamine. *tert.*-Butylcarbamide, $CMe_3\cdot NH\cdot CO\cdot NH_2$, has m. p. 183° (Schneegans gives 172°; compare A., 1894, i, 405); *phenyl*iso*propylcarbamide*, m. p. 191° (decomp.); *αα-diphenylethylcarbamide*, m. p. 206·5° (decomp.); *triphenylmethylcarbamide*, m. p. 234—235° (decomp.).

With carbon disulphide in cold ethereal solution, *tert.*-butylamine gives a *compound*, $C_9H_{22}N_2S_2$, which is probably a combination of the amine with *tert.*-butylthiosulphocarbamate. α-Phenyl*iso*propylamine reacts less readily, but gives a similar *compound*, whilst αα-diphenylethylamine reacts still more slowly, giving a poor yield of the alkylthiosulphocarbamate. Triphenylmethylamine does not react with carbon disulphide even at 100°. W. G.

Theory of Colour Lakes. I. OSKAR BAUDISCH (*Zeitsch. angew. Chem.*, 1917, **30**, I, 133—135).—It is shown that the lakes obtained with various nitrosoarylhydroxylamines can all be explained by Werner's theory, according to which they belong to the group of internal complex salts. The influence of the position of various groups, hydroxyl, nitro, carboxyl, sulphonic (SO_3H), and tolylsulphonyl ($-SO_2\cdot C_7H_7$), in the benzene and naphthalene nuclei is demonstrated by various examples. The pyrazolone and anthraquinone lakes are also shown to conform to Werner's theory.
T. S. P.

The Preparation of the Six Dichlorophenols and some of their Properties. A. F. HOLLEMAN (*Rec. trav. chim.*, 1917, **37**, 96—107).—The six dichlorophenols have been prepared, and from them the six dichloroanisoles and the odours of these compounds have been studied. The mixture of 2:4- and 2:6-dichlorophenol obtained in the chlorination of phenol may be readily separated by extraction with a dilute solution of sodium carbonate, the 2:6-dichlorophenol being removed. 2:3-*Dichlorophenol*, m. p. 57°, can be obtained by diazotising 2:3-dichloroaniline and pouring the product into boiling sulphuric acid (2 acid : 1 water). The anisoles were easily obtained from the corresponding phenols by Vermeulen's method (compare A., 1906, i, 256), using methyl sulphate. 2:3-*Dichloroanisole* has m. p. 31°, 2:4-*dichloroanisole*, m. p. 28°; 2:5-*dichloroanisole*, m. p. 24°; b. p. 140°/40 mm.; 2:6-*dichloroanisole*, m. p. 10·1°; 3:4-*dichloroanisole*, m. p. −8°; 3:5-*dichloroanisole*, m. p. 68°. 2:4-Dichlorophenol gives a *benzoyl* derivative, m. p. 96°, and an *amyl ether*, b. p. 172—173°/15 mm. 2:5-Dichlorophenol gives a *benzoyl* derivative, m. p. 69°.

The odours of these phenols and anisoles have been examined qualitatively, and in the case of the phenols quantitatively, the results being set out in detail in the original. W. G.

Colorimetric Studies of Picrate Solutions. WILLIAM M. DEHN and ALICE A. BALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1381—1392).—The colours of solutions of picric acid in 95% alcohol,

water, sodium hydroxide solution, and ammonia solution have been compared with those of solutions in absolute alcohol, and the concentrations of solutions of equal depths of colour are tabulated. It is found that 0·001% solutions in any medium have the same colour, but that in concentrated solutions the intensity of colour is as 1 : 3·1 : 10 : 22 5 : 24, the order being that of 100% alcohol, 95% alcohol, water, sodium hydroxide, and ammonia solution. The colours of the solutions are enhanced by raising the temperature.

These results are discussed on the basis of the white, benzenoid form of picric acid and the yellow, quinonoid form. White crystals of the acid, even in contact with pyrophosphoric acid, become yellow on treatment with alcohol or water. The change of configuration from benzenoid to quinonoid can, therefore, be brought about by solvents alone, even in the presence of hydrogen ions. Alcohol, water, alkalis, and heat have increasing effects on the rearrangement to the quinonoid type. It may be calculated that about 7860 molecules of water or 20,000 molecules of alcohol are necessary to ensure that every molecule of picric acid is quinonoid. The mechanism of the changes is discussed, and the various theories on the structure of picric acid and picrates are reviewed with extensive references to the literature. J. C. W.

The Crystalline Forms of the Two Naphthols. W. Stortenbeker (*Zeitsch. Kryst. Min.*, 1916, **55**, 373—374).—Groth and Negri state that α-naphthol is monoclinic, but the author confirms Wyroubov's statement that it is rhombic [0·6122 : 1 : 0·4236] (compare, however, H. Steinmetz, following abstract). The best crystals were obtained from a mixture of light petroleum and ether.

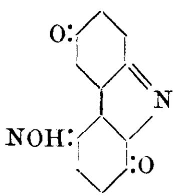
β-Naphthol crystallises in monoclinic plates [$a : b : c$ = 1·372 : 1 : 2·053 ; β = 60°10′]. The ratio $b : c$ appears uncertain, as it is calculated indirectly from a rare form {$\bar{5}\bar{2}5$}, which other observers have not detected. E. H. R.

The Crystalline Form of α-Naphthol. H. Steinmetz (*Zeitsch. Kryst. Min.*, 1916, **55**, 375).—A great many solvents were tried in an attempt to get good measurable crystals. The best results were obtained with a mixture of 1 part of acetic acid and 4 to 5 parts of light petroleum, saturated with α-naphthol at 25—30° and cooled slowly to 20°. The crystals obtained were thin plates, quite pure and white. They are monoclinic, prismatic [$a : b : c$ = 2·7483 : 1 : 2·7715 ; β = 117°10′]. E. H. R.

Preparation of Halogen Derivatives of Catechol, Homocatechol, and Pyrogallol Methyl Ethers and Sulphonic Acids Robert B. Krauss and Edward Crede (*J. Amer. Chem. Soc.*, 1917, **39**, 1431—1435).—Brief, practical details are given of the preparation of the following compounds: dibromoguaiacolsulphonic acid (*potassium* salt, $2H_2O$) and di-iodoguaiacolsulphonic acid (*sodium* salt, $2H_2O$) from guaiacolsulphonic acid; *bromocreosole*, $OMe{\cdot}C_6H_2MeBr{\cdot}OH$, large rhombs, m. p. 77°, from crude creosote,

b. p. 218—224°; pyrogallol 1:3-dimethyl ether and its sulphonic acid (*barium* salt, $3H_2O$); pyrogallol trimethyl ether sulphonic acid (*barium* salt, $2H_2O$); dibromopyrogallol sulphonic acid dimethyl ether (*sodium* salt, $2H_2O$); *dibromopyrogallol dimethyl ether*, prisms, m. p. 70°; and *dibromopyrogallol trimethyl ether*, m. p. 75—76°. J. C. W.

3 : 3′-Diphenol. W. Borsche (*Ber.*, 1917, **50**, 827—833. Compare Borsche and Scholten, this vol., i, 390).—By conversion into its tetrazo-derivative and subsequent treatment of this with alcohol and copper powder, benzidine-3:3′-disulphonic acid gave diphenyl-3:3′-disulphonic acid, which on fusion with potassium hydroxide at 250° gave 3:3′-diphenol. This substance (Schultz and Kohlhaus, A., 1906, i, 818), on reaction with nitrous acid, did not give the expected diquinonedioxime, but only a poor yield of a brown *substance*, $C_{12}H_6O_3N_2$, probably of the annexed constitution. When treated in alkaline solution with an aqueous solution of benzenediazonium chloride, 3:3′-diphenol was converted into 6:6′-*dibenzeneazo*-3:3′-*diphenol*,



$$N_2Ph{:}C_6H_3(OH){\cdot}C_6H_3(OH){:}N_2Ph,$$

deep yellow leaflets, m. p. 181°; this reacted with methyl sulphate in the presence of aqueous sodium hydroxide, forming its *dimethyl ether*, $C_{24}H_{18}O_2N_4$, red needles, m. p. 160°, and with alkaline sodium hyposulphite solution, yielding 6:6′-*diamino*-3:3′-*diphenol*,

$$NH_2{\cdot}C_6H_3(OH){\cdot}C_6H_3(OH){\cdot}NH_2,$$

colourless prisms, m. p. 225° (decomp.). In acetic acid solution 3:3′-diphenol reacted with nitric acid, giving 4:6:4′:6′-*tetranitro*-3:3′-*diphenol*, $OH{\cdot}C_6H_2(NO_2)_2{\cdot}C_6H_2(NO_2)_2{\cdot}OH$, yellow needles, m. p. 208·5°, together with a little 2:4:6:4′:6′-*pentanitro*-3:3′-*diphenol*, $OH{\cdot}C_6H(NO_2)_3{\cdot}C_6H_2(NO_2)_2{\cdot}OH$, yellow granules, m. p. 248° (decomp.); a much better yield of the tetranitro-compound was obtained on heating 3:3′-dichloro-4:6:4′:6′-tetranitrodiphenyl with sodium acetate and acetamide at 200°. The tetranitro- and pentanitro-compounds dissolve in aqueous alkalis and even in hot water, giving yellow solutions, from which they separate again on the addition of mineral acids.

2:4:6:2′:4′:6′-*Hexanitro*-3:3′-*diphenol*,

$$OH{\cdot}C_6H(NO_2)_3{\cdot}C_6H(NO_2)_3{\cdot}OH,$$

yellow, silky needles, m. p. with explosion above 270°, was obtained by the conjoint action of sulphuric acid and nitric acid on 3:3′-diphenol, which also reacted with bromine in acetic acid solution in the presence of a little iron as catalyst with the formation of *hexabromo*-3:3′-*diphenol*, $C_{12}H_4O_2Br_6$, colourless needles, m. p. 196°. D. F. T.

The State of Saturation of Chromophores. I. Lifschitz (*Ber.*, 1917, **50**, 906—909. Compare Kauffmann, this vol., i, 391).—A reply to Kauffmann's criticisms. J. C. W.

The Identification of Acids. III. EDWARD LYONS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1727—1750. Compare this vol., i, 334).—The application of *p*-nitrobenzyl bromide as a reagent for the identification of acids has been extended to a number of other acids, excellent results being obtained with most of the aromatic acids. Several mixtures of acids have been investigated by this method, and it is found that benzoic acid is readily identified in the presence of acetic, tartaric, citric, salicylic, and *p*-toluenesulphonic acids, and that the sparingly soluble *p*-nitrobenzyl ester of *iso*phthalic acid is readily separable from the acetate, benzoate, and tartrate. The melting points of the esters now described are as follows: *bromoacetate*, 88—89°; *diphenylhydroxyacetate*, 99·5°; *α-amino-*n*-hexoate*, 184—185°; *α-amino-β-phenylpropionate*, 221·5°; *α-aminopropionate*, 228—230°; *laevulinate*, 60·5—61°; *hydroxy*iso*butyrate*, 80·5°; *α-amino-*n*-butyrate*, 222—223°; *urate*, $C_5H_3O_3N_4\cdot CH_2\cdot C_6H_4\cdot NO_2$ (?), above 305°; *pyromucate*, $C_4H_3O\cdot CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2$ (?), 133·5°; *cyanurate*, $C_3H_2O_3N_3\cdot CH_2\cdot C_6H_4\cdot NO_2$ (?), 284°; *stearate*,

$$CH_3\cdot[CH_2]_{16}\cdot CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2 \ (?),$$

above 285°; *palmitate*, 42·5°; *chlorofumarate*, 138·5°; dibromosuccinate, 177·5°; *mucate*, above 310°; *camphorate*, 66·5°; p-*chlorobenzoate*, 129·5°; m-*bromobenzoate*, 104·5°; m-*nitrobenzoate*, 141·5°; p-*nitrobenzoate*, 168·5°; *m*-aminobenzoate, 201°; 2:5-*dihydroxybenzoate*, 160°; 2:4-*dihydroxybenzoate*, 188—189°; m-*acetylaminobenzoate*, 169·5—170°; m-*acetoxybenzoate*, 140°; p-*toluate*, 104·5°; p-*thioltoluate*, 97°; o-, m-, and p-*creosotates*, 98·5°, 174°, and 147° respectively; 5-*iodosalicylate*, 141°; 5-*aminosalicylate*, 200·5°; *o*-acetoxybenzoate, 90·5°; *anisate*, 132°; *vanillate*, 140—141°; *piperate*, 145°; o-, m-, and p-*nitrocinnamates*, 132°, 174°, and 186·5° respectively; *coumarate*, 152·5°; *β-hydroxynaphthoate*, 164°; o-*benzoicsulphinide* derivative,

$$C_6H_4{<}{\substack{CO\\SO_2}}{>}N\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

174·5°; *iso*phthalate, 202·5°; *terephthalate*, 263·5°; 4:5-*dichlorophthalate*, 164·5°; *tetrachlorophthalate*, 180°; 3-*nitrophthalate*, 189·5°; *mellitate*, $C_6(CO_2\cdot CH_2\cdot C_6H_4\cdot NO_2)_6$ (?), 300°. T. H. P.

The Ferrous Sulphate and Ammonia Method for the Reduction of Nitro- to Amino-compounds. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1435—1439).—The authors advocate the wider application of the ferrous sulphate and ammonia method for reducing nitro-compounds, and quote examples of amino-derivatives which are conveniently obtained in this way. These include *m*- and *p*-aminophenylacetic acids; *p*-aminophenoxyacetic acid,

$$NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

m. p. 220° (evolution of gas, re-solidification; residue not molten at 285°); *o*-aminobenzamide, m. p. 109—111·5°; m-*aminobenzamide*, silky needles, m. p. 113—114° (corr.); *o*-aminobenzoylcarbamide, pale yellow leaflets, comparatively stable in boiling acetic acid (com-

pare Diels and Wagner, A., 1912, i, 512); and *m*-aminobenzoylcarbamide, which melts at 210° with evolution of gas, resolidifies, and melts again at 275—280°, and is diazotisable. J. C. W.

The Action of Alcoholic Ammonia on some Alkylurethanes [Carbamates]. M. BRANDER (*Rec. trav. chim.*, 1917, **37**, 88—91).—The carbamates examined were prepared by the action of ethyl chloroformate in ethereal solution on the four primary amines previously described (this vol., i, 555). *Ethyl α-phenyl*iso*propylcarbamate*, $CPhMe_2\cdot NH\cdot CO_2Et$, crystallises in needles, m. p. 52°; *ethyl αα-diphenylethylcarbamate*, slender needles, has m. p. 66·5°; and *ethyl triphenylmethylcarbamate* has m. p. 112°.

Ethyl *tert.*-butylcarbamate (compare van Erp, A., 1895, i, 587), when heated for twelve hours at 180—185° in a sealed tube with alcoholic ammonia, gives *tert.*-butylamine hydrochloride, ethyl carbamate, carbamide, and a trace of *tert.*-butylcarbamide. Ethyl α-phenyl*iso*propylcarbamate behaves similarly, but gives a larger yield of α-phenyl*iso*propylcarbamide. Ethyl αα-diphenylethylcarbamate gives none of the corresponding carbamide, whereas ethyl triphenylmethylcarbamate gives a considerable amount of triphenylmethylcarbamide. W. G.

The Action of Sodium Hypochlorite on Amides of Unsaturated Acids. R. A. WEERMAN (*Rec. trav. chim.*, 1917, **37**, 1—15).—An extension of previous work (compare A., 1913, i, 1195), four other amides having been studied.

The addition of sodium hypochlorite to a solution of *p*-methoxycinnamamide in methyl alcohol yielded *methyl* p-*methoxystyrylcarbamate*, colourless needles, m. p. 134—135°, which when moistened with dilute sulphuric acid and distilled in a current of steam gave *p*-methoxyphenylacetaldehyde. *o*-Methoxycoumaramide yielded *methyl* trans-o-*methoxystyrylcarbamate*, colourless needles, m. p. 114—115°, giving o-*methoxyphenylacetaldehyde*, a colourless oil, b. p. 115—117°/17 mm., yielding an *oxime*, m. p. 94—95°, and a *semicarbazone*, m. p. 158—159°. *o*-Methoxycoumarinamide gave *methyl* cis-o-*methoxystyrylcarbamate*, m. p. 39—40°, from which *o*-methoxyphenylacetaldehyde can also be prepared. o-*Coumaramide*, rectangular plates, m. p. 208—209°, obtained by the action of ammonia on methyl *o*-coumarate, gave nothing but resinified products under the action of sodium hypochlorite. W. G.

Camphoceanaldehydic Acid (*tert.-sec.*) (**Camphoric Acid Semialdehyde).** J. BREDT (*J. pr. Chem.*, 1917, [ii], **95**, 63—74). —When fused with potassium hydroxide and a little water, active or racemic camphorquinone gives a violet-coloured mass, which subsequently becomes colourless; if the heating is discontinued as soon as a small sample of the mixture gives a clear solution in water, the semi-aldehyde of camphoric acid (camphoraldehydic acid) is obtained in good yield, the chemical change probably occurring by the stages

$$C_8H_{14}\Big<{\genfrac{}{}{0pt}{}{CO}{CO}} \rightarrow C_8H_{14}\Big<{\genfrac{}{}{0pt}{}{C(OH)OK}{CO}} \rightarrow C_8H_{14}\Big<{\genfrac{}{}{0pt}{}{CHO}{CO_2K}}.$$

As electrolytic reduction of the product yielded a hydroxy*iso*campholic acid, the dehydration of which produced β-campholide, the aldehyde and carboxyl groups in the semialdehyde must be situated at the tertiary and secondary carbon atoms respectively, thus:

$$\begin{matrix} CH_2\text{-}CH(CO_2H) \\ | \\ CH_2\cdot CMe(CHO) \end{matrix}\!\!>\!CMe_2.$$

dl-*Camphorquinone*, m. p. 199°, prepared by the successive action of sodium–potassium amide and amyl nitrite on *dl*-camphor in the presence of benzene, on fusion with a mixture of equal weights of potassium hydroxide and water at 280—290°, yielded dl-*camphoraldehydic acid*, m. p. 61—64°; *oxime*, m. p. 148—149°; when heated with acetic anhydride at 100° for three to four hours, the aldehyde acid gave dl-*acetoxy-β-campholide*, $C_8H_{14}<\begin{matrix}CO\text{------}\\CH(OAc)\end{matrix}>O$, m. p. 97—98°, b. p. 155—156°/4 mm., whilst electrolytic reduction in potassium carbonate solution at a potassium amalgam cathode converted it into dl-*β-campholide*, m. p. 216—217°.

In a similar manner *d*-camphorquinone was made to yield d-*camphoraldehydic acid*, m. p. 74—80°; $[\alpha]_D^{18}$ +80·4° in methyl alcohol, +103·0° in benzene; *oxime*, m. p. 153—155°, b. p. 165°/3 mm., $[\alpha]_D^{18}$ +55·67° in methyl alcohol; *semicarbazone*, m. p. 195—196° (decomp.). The aldehyde-acid with acetic anhydride yielded l-*acetoxy-β-campholide*, m. p. 124—125°, $[\alpha]_D^{18}$ −78·3° in benzene, and on reduction gave *d*-β-campholide, m. p. 216—217°, $[\alpha]_D^{18}$ +35·6° in methyl alcohol, +46·08° in benzene (compare Haller and Blanc, A., 1905, i, 858).

The indefinite m. p.'s of the active and racemic forms of camphoraldehydic acid are probably to be attributed to the presence of *cis-trans*-isomerides.

dl-*α-Campholide*, m. p. 210—211°, was obtained by oxidation of *dl*-camphor with potassium persulphate. The active and inactive modifications of α-campholide are readily distinguished from the β-campholides by the fact that they react with an acetic acid solution of hydrogen bromide, yielding bromocampholic acid, whereas the β-isomerides are unaffected. D. F. T.

The Crystalline Form of Phenylglyceric Acid and its Active Components. V. M. GOLDSCHMIDT (*Zeitsch. Kryst. Min.*, 1915, **55**, 123—131).—Inactive phenylglyceric acid melts at 141°, whilst its lævo- and dextro-components melt at 164—165°. An examination of the crystals of the active and inactive forms of the acid has been made with the object of determining whether the latter is a true or pseudo-racemic compound.

The crystals of the *d*- and *l*-active forms belong to the monoclinic-sphenoidal class, and are enantiomorphous, but otherwise identical. The axial ratios are $[a:b:c = 2·1875:1:2·0794;\ \beta = 93°53']$, D 1·451, and the crystals have a good cleavage parallel to {100} and less perfect cleavages parallel to {001} and {110}. Their enantiomorphous character is clearly shown by etching with methyl alcohol.

The crystals of the inactive form are similar in habit to those of

the active form, have the same density and axial ratios, but appear to belong to the prismatic class of the monoclinic system, since the faces which reveal the enantiomorphous character of the active crystals are lacking. The etched figures, however, are of the same enantiomorphous character as those of the active crystals, and indicate clearly that the inactive crystals are made up of parallel layers on the face {100} of equal quantities of the right- and left-handed crystals. This conclusion was confirmed by crystallising the inactive acid from various solvents, when sometimes active right- and left-handed crystals were obtained.

The lower melting point of the inactive acid is in agreement with Roozeboom's generalisation, that the melting-point curve of a system of optical antipodes which form neither true mixed crystals nor a true racemic compound must show a temperature minimum with equal quantities of the two antipodes. The author has examined the melting-point curve of mixtures of *d*- and *l*-phenylglyceric acids, and finds a minimum at 141° with 50% of each component.

It is suggested that pseudo-racemic crystals should be divided into two classes:

A. Pseudo-racemic mixed crystals, that is, isomorphous mixtures of equal quantities of *d*- and *l*-substance, the melting-point curve varying continuously, as in camphoroxime.

B. Pseudo-racemic conglomerates, lamellar growths of equal quantities of both antipodes, an example of which we have in phenylglyceric acid. E. H. R.

Resolution of the Phenylglyceric Acid with m. p. 122° into its Optically-active Components. C. N. RIIBER and E. BERNER (*Ber.*, 1917, **50**, 893—897).—Two years ago the resolution of phenylglyceric acid of m. p. 141° was described (A., 1915, i, 544), and it was then assumed that the acid with m. p. 122° had already been resolved by Plöchl and Mayer (A., 1897, i, 528). It has now been found that these authors were in error. They reported that their active acids of m. p. 167° did not unite to form the racemeride, but the new acids of m. p. 95° are found to do so in the normal way. Transformation into the active components of the acid with m. p. 141° must have taken place.

Phenylglyceric acid, m. p. 122°, is resolved by taking advantage of the fact that the strychnine salt of the *d*-acid is the less soluble in alcohol. The *d*-acid has m. p. 95°, $[\alpha]_D^{20}$ +26·11°, $[\alpha]_C^{20}$ +20·19°, $[\alpha]_E^{20}$ +34·48° in water, $[\alpha]_D^{20}$ +21·15° in 97% alcohol, $[\alpha]_D^{20}$ +27·49° in acetone, and crystallises in needles, tablets, or prisms of the monoclinic–sphenoidal class [$a:b:c=2·5408:1:2·2216$; $\beta=90°40'$]. The *l*-acid has m. p. 97—98°, $[\alpha]_D^{20}$ −25·6°.

The racemic acid, m. p. 122°, exists in two enantiomorphous forms [$a:b:c=2·5605:1:1·7251$; $\beta=101°27'$].

The following table gives the number of grams of the acids which dissolve in 100 grams of dry ether at 20°:

	Inactive.	*d*-Acid.	*l*-Acid.
Phenylglyceric acid, m. p. 122° ...	2·78	9·02	—
Phenylglyceric acid, m. p. 141° ...	1·08	0·80	0·48

J. C. W.

n- **and** *iso***Propylamine.** S. GABRIEL and HEINZ OHLE (*Ber.*, 1917, **50**, 804—818).—An endeavour to convert β-chloro-*n*-propyl alcohol into the corresponding hydroxy*iso*propylamine by the potassium phthalimide method unexpectedly gave rise to the *n*-propylamine compound. This is found to be due to the primary elimination of hydrogen chloride from the halogen compound under the influence of the potassium phthalimide with the formation of propylene oxide, which then reacts additively with the phthalimide, giving a product of the constitution

$$CH_3\cdot CH(OH)\cdot CH_2\cdot N{<}{}^{CO}_{CO}{>}C_6H_4$$

(see following abstract). A similar observation that β-chloro-*n*-propyl acetate likewise yielded the phthalimide derivative corresponding with β-acetoxy-*n*-propylamine is attributed to the presence of some chloro*iso*propyl acetate in the original β-chloro-*n*-propyl acetate, again probably due to the partial intermediate formation of propylene oxide during the treatment of chloro*iso*propyl alcohol with potassium acetate, the unaltered compound yielding acetoxy*iso*-propyl alcohol, whereas the propylene oxide combines with acetic acid, giving rise to β-acetoxy-*n*-propyl alcohol; when this mixture is submitted to the action of hydrogen chloride, a mixture of two chloro-isomerides is obtained, which have almost the same b. p. and are not easily separable by distillation. In an attempt to obtain the desired chlorohydroxypropane derivatives in a pure condition, chloro*iso*propyl alcohol was made to react with potassium benzoate and the hydroxyl group of the product was then displaced by bromine in the hope of obtaining solid substances purifiable by crystallisation; the products, however, were liquids, and investigation showed that in these the benzoyloxy-group was present to a considerable extent at the β-position, this result again indicating the intermediate occurrence of propylene oxide.

β-Hydroxy-*n*-propylphthalimide has m. p. 88—90° (Mendelssohn-Bartholdy, A., 1907, i, 1043, gives m. p. 73°), whether prepared from β-chloro*iso*propyl alcohol or β-chloro-*n*-propyl alcohol. *β-Acetoxy-*n*-propylphthalimide*, $OAc\cdot CHMe\cdot CH_2\cdot N{<}{}^{CO}_{CO}{>}C_6H_4$, needles, m. p. 99—100°, obtained by the interaction of potassium phthalimide and Henry's "β-chloro-*n*-propyl acetate" (A., 1903, i, 725), on hydrolysis gave α-amino*iso*propyl alcohol (*hydrochloride*, m. p. 72·5—74°; *sodium picrate*, $OH\cdot C_3H_6\cdot NH_2,C_6H_3O_7N_3,C_6H_2O_7N_3Na$, m. p. 177—178°). β-Benzoyloxy-*n*-propylphthalimide,

$$OBz\cdot CHMe\cdot CH_2\cdot N{<}{}^{CO}_{CO}{>}C_6H_4,$$

leaflets, m. p. 115—116°, obtained by the successive action of potassium benzoate, hydrobromic acid, and potassium phthalimide on β-chloro*iso*propyl alcohol, can also be formed from β-hydroxy-*n*-propylphthalimide by treating with hydrobromic acid and potassium benzoate successively. Hydrolysis of β-benzoyloxy-*n*-propylphthalimide with hydrochloric acid in solution in acetic acid yields *β-chloro-*n*-propylamine*, $CHMeCl\cdot CH_2\cdot NH_2$ (*hydrochloride*, crystalline powder, m. p. 183·5—186°; *picrate*, rhombic tablets and cubes,

m. p. 154·5—155·5°; *platinichloride*, needles, m. p. 221—225°, decomp.); the hydrochloride of this base, when heated with phthalic anhydride, is converted into β-chloro-*n*-propylphthalimide,

$$CHMeCl\cdot CH_2\cdot N{<}{}^{CO}_{CO}{>}C_6H_4,$$

needles, m. p. 100—102°, identical with the product of interaction between β-hydroxy-*n*-propylphthalimide (above) and phosphorus pentachloride. The hydrolysis of β-benzoyloxy-*n*-propylphthalimide can also be so conducted as to give rise to α-amino*iso*propyl alcohol.

β-*Hydroxy*iso*propylphthalimide*, $C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CHMe\cdot CH_2\cdot OH$, long, hexagonal leaflets, m. p. 99—101°, obtained by the action of phthalic anhydride on an alcoholic solution of β-amino-*n*-propyl alcohol (hydroxy*iso*propylamine), reacts with phosphorus pentachloride, giving β-*chloro*iso*propylphthalimide*,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CHMe\cdot CH_2Cl,$$

leaflets, m. p. 56—58°, and with phosphorus pentabromide yielding the corresponding β-*bromo*-derivative, tablets, m. p. 59—60°.

β-Bromo*iso*propylamine hydrobromide when treated in hot aqueous solution with potassium thiocyanate, undergoes conversion into 2-*amino*-4-*methylthiazoline hydrobromide*,

$$\begin{matrix}CHMe\cdot N\\ |\\ CH_2\text{---}S\end{matrix}{>}C\cdot NH_2,HBr,$$

needles, m. p. 128—129° (*picrate*, yellow, crystalline powder, m. p. 230—244°, decomp.), whilst on treatment with a solution of sodium hydroxide (2 molecules) and with carbon disulphide (1 molecule) successively, it gives rise to 2-*thiol*-4-*methylthiazoline*

$$\begin{matrix}CHMe\cdot N\\ |\\ CH_2\text{---}S\end{matrix}{>}C\cdot SH,$$

rhombic needles and leaflets, m. p. 98·5—99°.

Contrary to the belief of Gabriel and von Hirsch (A., 1897, i, 135), β-bromopropylamine and β-bromo*iso*propylamine, when made to eliminate hydrogen bromide and then to recombine with this compound, both yield β-bromo*iso*propylamine, this result being explicable by the intermediate compound being propyleneimine, $\begin{matrix}CHMe\\ |\\ CH_2\text{---}\end{matrix}{>}NH$, and not *iso*allylamine, $CHMe{:}CH\cdot NH_2$. In a similar manner, the products of the action of hydrogen chloride and hydrogen iodide on the propyleneimine are to be regarded as β-chloro*iso*propylamine and β-iodo*iso*propylamine, the picrate of the former having m. p. 145—146° (Gabriel and von Hirsch, *loc. cit.*, give m. p. 158°). The identity of the intermediate compound as propyleneimine, and not *iso*allylamine, is further confirmed by a demonstration that the additive compound with sodium hydrogen sulphite is not β-methyltaurine, m. p. 290—293° (Gabriel and Colman, A., 1906, i, 889), but has m. p. 323° (decomp.), and is

actually *iso*propylamine-β-sulphonic acid, whilst the carbon disulphide additive compound is 2-thiol-4-methylthiazoline,

$$\begin{matrix} CHMe\cdot N \\ | \\ CH_2\text{---}S \end{matrix}\!\!>\!C\cdot SH,$$

and not the 2-thiol-5-methyl isomeride. D. F. T.

Preparation of Primary Alkylamines. S. GABRIEL and HEINZ OHLE (*Ber.*, 1917, **50**, 819—825. Compare preceding abstract).—Whereas ethylene oxide and its homologues react with ammonia, yielding a mixture of primary, secondary, and tertiary alkylamines, it is possible to effect the combination of these oxides with phthalimide, with the formation of products from which a pure primary alkylamine can be obtained by hydrolysis.

Ethylene oxide and propylene oxide in this way give rise to β-hydroxyethylphthalimide and β-hydroxypropylphthalimide respectively. Epichlorohydrin yields *γ-chloro-β-hydroxypropylphthalimide*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot N{<}^{CO}_{CO}{>}C_6H_4$, a colourless, crystalline powder, m. p. 95—96·5°, the constitution of which is indicated by its further conversion into $\beta\gamma$-dichloropropylphthalimide on treatment with phosphorus pentachloride, and into β-hydroxytrimethylenediphthalimide by further treatment with potassium phthalimide. γ-Chloro-β-hydroxypropylphthalimide reacts with alcoholic sodium iodide, giving rise to *γ-iodo-β-hydroxypropylphthalimide*, $CH_2I\cdot CH(OH)\cdot CH_2\cdot N{<}^{CO}_{CO}{>}C_6H_4$, needles, m. p. 123—124°; when warmed with potassium hydroxide solution and then treated with sodium nitrite and hydrochloric acid, it is converted into the *nitrosoamine* of *$\beta\gamma$-dihydroxypropylphthalamic anhydride*, $C_6H_4{<}^{CO\text{---}O\text{---}CH_2}_{CO\cdot N(NO)\cdot CH_2}{>}CH\cdot OH$, prisms, m. p. 104° (compare Gabriel, A., 1905, i, 650); chromic acid effects its oxidation to *γ-chloroacetonylphthalimide*,

$$CH_2Cl\cdot CO\cdot CH_2\cdot N{<}^{CO}_{CO}{>}C_6H_4,$$

needles, m. p. 139·5°, whilst hydrochloric acid causes its hydrolysis to β-chloro-β'-amino*iso*propyl alcohol; *hydrochloride*, leaflets, m. p. 103—104°; *picrate*, m. p. 159·5—160·5°; *platinichloride*, needles, m. p. 214—216° (decomp.); the *benzoyl* derivative, leaflets, m. p. 103°, on boiling with water is converted into oily *γ-amino-β-hydroxypropyl benzoate*, $OBz\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2$ (*hydrochloride*, crystals, m. p. 164·5°; *aurichloride* and *platinichloride*, crystalline), whilst when boiled with aqueous potassium hydroxide it yields *5-hydroxy-2-phenylpentoxazoline*, $CPh{<}^{N\cdot CH_2}_{O\cdot CH_2}{>}CH\cdot OH$, needles, m. p. 98°.

The interaction of glycide and phthalimide at 120—130° produces *$\beta\gamma$-dihydroxypropylphthalimide*,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot N{<}^{CO}_{CO}{>}C_6H_4,$$

leaflets, m. p. 111·5—112·5°, which reacts with hydrobromic acid at 170°, giving βγ-dibromopropylamine hydrobromide, and at 100° forming *γ-bromo-β-hydroxypropylphthalimide*,

$$CH_2Br\cdot CH(OH)\cdot CH_2\cdot N{<}{\overset{CO}{\underset{CO}{}}}{>}C_6H_4,$$

m. p. 114—114·5°; this on treatment with potassium phthalimide yields β-hydroxytrimethylenediphthalimide. D. F. T.

The *cyclo*Propane Series. E. P. KOHLER and J. B. CONANT (*J. Amer. Chem. Soc.*, 1917, **39**, 1404—1420).—An account of the reactions of compounds of the type $(CO_2R)_2\overset{1}{C}{<}\begin{matrix}\overset{2}{C}HPh\\ |\\ \underset{3}{C}HBz\end{matrix}$. In some respects, notably in their stability towards permanganate, ozone, or bromine, these compounds behave quite differently from ethylenes, but in others they resemble αβ-unsaturated ketones and acids, particularly in being attacked very readily by halogen hydrides, nascent hydrogen, bases, and metallic derivatives. With these agents, it is possible to effect a rupture of the ring at each of the three points. Nascent hydrogen opens the ring between atoms 1 and 3, alkyl oxides, ammonia, and amines rupture the ring between 1 and 2, and halogen hydrides dissolved in glacial acetic acid attack the 2:3-position. These reactions show that a *cyclo*propane ring and a ketonic group in the above juxtaposition behave like a conjugate system.

The particular substance from which the present *cyclo*propane derivatives were obtained was methyl γ-benzoyl-β-phenylethylmalonate (A., 1911, i, 984). This is best prepared by adding sodium methoxide solution to a mixture of phenyl styryl ketone and methyl malonate until the reaction is just distinctly alkaline. The ester forms two isomeric bromides (*ibid.*),

$$COPh\cdot CHBr\cdot CHPh\cdot CH(CO_2Me)_2;$$

the one with m. p. 113° is best formed by brominating in chloroform at −10°, the other, m. p. 98°, by exposing a suspension of the ester in dry methyl alcohol and bromine to sunlight. Many substances remove the elements of hydrogen bromide from these compounds, with the formation of stereoisomeric *cyclo*propane derivatives, but a slight excess of magnesium methoxide gives the purest products. *Methyl 3-benzoyl-2-phenyl*cyclo*propanedicarboxylate* crystallises in large tablets, m. p. 72° (from the bromide with m. p. 98°), or plates, m. p. 92° (from the less fusible bromide). The compound previously considered to be methyl γ-benzoyl-β-phenylvinylmalonate was really the *cyclo*propane derivative, m. p. 92°.

The two esters are hydrolysed to the same *methyl hydrogen* ester (needles from diluted methyl alcohol, large prisms from chloroform, m. p. 155°) by leaving an ethereal solution in contact with a slight excess of sodium methoxide for a few minutes. This ester yields the di-ester, m. p. 72°, when re-esterified, and may be further hydrolysed by alcoholic potassium hydroxide to *γ-benzoyl-*

*β-phenyl*cyclo*propanedicarboxylic acid*, which is best obtained in the two stages, and was originally supposed to be γ-benzoyl-β-phenylbutyrolactonic acid.

The dimethyl esters suffer rupture of the ring when treated with anhydrous alkaline agents, but partial hydrolysis usually happens as well. Magnesium methoxide gives the best results. When a solution of either ester in dry methyl alcohol is boiled with this agent as long as the yellow magnesium compound which is formed seems to increase, it yields *methyl β-benzoyl-γ-phenylvinylmalonate*, $CHPh{:}CBz{\cdot}CH(CO_2Me)_2$, in plates, m. p. 119°, whilst a geometric *isomeride*, m. p. 147°, is produced if the action is prolonged to some hours. These esters yield the same *γ-hydroxy-β-benzoyl-γ-phenylethylmalonic acid*,

$$OH{\cdot}CHPh{\cdot}CHBz{\cdot}CH(CO_2H)_2,$$

on addition to 20% sodium hydroxide and boiling for a few minutes. The acid crystallises in long, slender needles, m. p. 125° (decomp.), yields the ester with m. p. 147° when esterified, is decomposed into benzaldehyde and β-benzoylpropionic acid if boiled too long with water or bases, and gives β-benzoyl-γ-phenyl*iso*crotonic acid (β-benzoyl-β-benzylidenepropionic acid),

$$CHPh{:}CBz{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 131° (compare Borsche, A., 1914, i, 686), on heating at 100° for a few hours. The two esters also behave alike towards permanganate. In moist acetone they yield benzoic acid and carbon dioxide, but in dry acetone they take up one atomic proportion of oxygen only, and form a sparingly soluble *substance*, m. p. 220° (decomp.).

γ-Benzoyl-β-phenyl*cyclo*propanedicarboxylic acid reacts with a solution of hydrogen bromide in glacial acetic acid when left in the cold for some weeks to form the above β-benzoyl-γ-phenyl*iso*crotonic acid (I) and yellow α-benzylidene-γ-phenylcrotonolactone (II), m. p. 150° (*ibid.*), which are separated by fractional crystallisation. These are obviously secondary products, but the production of the first can be traced to a rupture of the ring between carbon atoms 1 and 2, and that of the second to an attack between 2 and 3, thus:

$$(CO_2H)_2C<\begin{matrix}CHPh\\ |\\ CHBz\end{matrix} + HBr \longrightarrow CHPhBr{\cdot}CHBz{\cdot}CH(CO_2H)_2$$

$$\downarrow$$

$$CHPh{:}CBz{\cdot}CH_2{\cdot}CO_2H + CO_2 + HBr$$

(I.)

$$\longrightarrow CHPhBr{\cdot}C(CO_2H)_2{\cdot}CH{:}CPh{\cdot}OH$$

$$\downarrow$$

$$CHPhBr{\cdot}C(CO_2H)<\begin{matrix}CH{:}CPh\\ \qquad |\\ CO{-}O\end{matrix} + H_2O$$

$$\downarrow$$

$$CHPh{:}C<\begin{matrix}CH{:}CPh\\ \qquad |\\ CO{-}O\end{matrix} + CO_2 + HBr$$

(II.)

The action of heat on γ-benzoyl-β-phenyl*cyclo*propanedicarboxylic acid was investigated earlier, but the results were misinterpreted. Six products have been separated and identified, namely: (1) the above benzoylphenyl*iso*crotonic acid, previously called benzoylphenylvinylacetic acid; (2) an α-phenacylcinnamic acid, m. p. 180°; (3) *3-benzoyl-2-phenyl*cyclo*propane-1-carboxylic acid*, long, silky needles, m. p. 150°; (4) and (5) isomeric α-benzylidene-γ-phenylcrotonolactones, m. p. 150° and 180°, both yellow; and (6) β-benzoyl-γ-phenylbutyrolactone, m. p. 93°. Three distinct reactions are involved in the production of these compounds.

The various *cyclo*propane derivatives are readily reduced by means of zinc dust and acetic acid to the esters of γ-benzoyl-β-phenylethylmalonic acid, or the acid itself, as the case may be.

J. C. W.

The *cyclo***Propane Series. II.** E. P. KOHLER and J. B. CONANT (*J. Amer. Chem. Soc.*, 1917, **39**, 1699—1715).—Further investigations (compare preceding abstract) have been made with methyl 3-benzoyl-2-*m*-bromo-*p*-methoxyphenyl*cyclo*propane-1:1-dicarboxylate and its derivatives. The results show that the ring in these compounds is more or less easily opened by reducing agents, halogen hydracids, bases, the Grignard reagent, or phosphorus pentachloride, and that it is possible to open the ring in three different ways. The primary reaction between the *cyclo*propane derivative and any reagent is similar to that between the corresponding ethylenic compound and the same reagent. These *cyclo*propane derivatives exhibit, indeed, all the peculiarities of ethylenic compounds containing conjugated systems of double linkings, but they do not, like many ethylenic compounds, combine with the halogens or reduce permanganate.

Addition of methyl malonate to phenyl *p*-methoxystyryl ketone yields *methyl* γ-*benzoyl*-β-*4-methoxyphenylethylmalonate*,

$$OMe{\cdot}C_6H_4{\cdot}CH(CH_2Bz){\cdot}CH(CO_2Me)_2,$$

m. p. 80°, or (+1Et·OH), 66°, or (+1Me·OH), 58°, but the *cyclo*propane compound could not be obtained from this compound.

Phenyl m-*bromo*-p-*methoxystyryl ketone*,

$$OMe{\cdot}C_6H_3Br{\cdot}CH{:}CHBz,$$

prepared from bromoanisaldehyde and acetophenone in the presence of sodium hydroxide, forms yellow needles, m. p. 107°, and unites with two atoms of bromine, giving *phenyl* $\alpha\beta$-*dibromo*-β-m-*bromo*-p-*methoxyphenylethyl ketone*, m. p. 179°. Addition of the unsaturated ketone to methyl malonate yields *methyl* γ-*benzoyl*-β-*3-bromo-4-methoxyphenylethylmalonate*,

$$OMe{\cdot}C_6H_3Br{\cdot}CH(CH_2Bz){\cdot}CH(CO_2Me)_2,$$

which forms slender, white needles, m. p. 125°; the corresponding *potassium* salt decomposes at 185°. The action of bromine on the malonic derivative yields an oily bromo-compound, which, when boiled with potassium acetate in methyl-alcoholic solution, is converted into *methyl 3-benzoyl-2-*m-*bromo*-p-*methoxyphenyl*cyclo*propane-1:1-dicarboxylate*, $CHBz{<}\begin{matrix}CH{\cdot}C_6H_3Br{\cdot}OMe\\ |\\ C(CO_2Me)_2\end{matrix}$, which forms

long needles, m. p. 153°. Reduction of this ester by means of zinc dust and acetic acid gives the original saturated ketonic ester. The corresponding *methyl hydrogen ester*, $C_{20}H_{17}O_6Br$, forms needles, m. p. 178° (decomp.), and the acid, $C_{18}H_{15}O_6Br$, has m. p. 210—220° (decomp.).

The action of calcium or magnesium methoxide on the methyl ester yields: (1) an *isomeric* cyclo*propane* ester, needles, m. p. 129°, and (2) *methyl β-benzoyl-γ-3-bromo-4-methoxyphenylvinylmalonate*, $OMe{\cdot}C_6H_3Br{\cdot}CH{:}CBz{\cdot}CH(CO_2Me)_2$, cubical crystals, m. p. 129°, and an isomeric unsaturated *ester*, needles, m. p. 139°. In acetone containing a little water or acetic acid, these two unsaturated esters are rapidly oxidised by permanganate to benzoic and bromoanisic acids, whereas in absence of water the product is a crystalline *substance*, m. p. 245° (decomp.), which was not further investigated. Hydrolysis of the esters gives *γ-hydroxy-β-benzoyl-γ-3-bromo-4-methoxyphenylethylmalonic acid*,

$$OMe{\cdot}C_6H_3Br{\cdot}CH(OH){\cdot}CHBz{\cdot}CH(CO_2H)_2,$$

m. p. 144°. When boiled with water, the latter loses water and carbon dioxide, giving *β-benzoyl-γ-3-bromo-4-methoxyphenylvinylacetic acid*, $OMe{\cdot}C_6H_3Br{\cdot}CH{:}CBz{\cdot}CH_2{\cdot}CO_2H$, m. p. 178—180°, which rapidly reduces permanganate, but does not combine with bromine, and may also be obtained synthetically from methyl β-benzoylpropionate and bromoanisaldehyde.

When phenyl α-bromo-β-phenylethyl ketone is treated with ethyl sodiomalonate and the resulting unsaturated ketone reduced with hydrogen in the presence of colloidal palladium, the saturated ketone so produced treated with bromine, and the product condensed with methyl sodiomalonate, an oil is obtained which, when shaken with sodium methoxide and the product acidified, gives a colourless solid, m. p. 116°, which may be the *lactone*,

$$\begin{array}{l}CH(C_6H_3Br{\cdot}OMe){\cdot}CH{:}CPh \\ \vert \qquad\qquad\qquad\qquad\qquad\quad \vert \\ CH(CO_2Me)\text{——}CO\text{——}O\end{array}.$$

The above *cyclo*propane esters or acids are attacked by hydrobromic acid in glacial acetic acid, the ring being opened between the 1- and 2-carbon atoms and the *acid*,

$$OMe{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CHBz{\cdot}CH(CO_2H)_2,$$

formed. When heated with a dilute acid, the calcium salt of this acid gives an oily lactone, which is converted by methyl-alcoholic potassium hydroxide into the monobasic unsaturated acid, m. p. 178° (see above), and a minute quantity of the acid, m. p. 155—156°.

The action of phosphorus pentachloride on the *cyclo*propane acid yields the *lactone*, $OMe{\cdot}C_6H_3Br{\cdot}CH{:}C{<}\begin{array}{l}CH{:}C\\ CO{-}O\end{array}$, canary-yellow needles, m. p. 197°, which may also be prepared by heating a mixture of sodium γ-phenyl*iso*crotonate, bromoanisaldehyde, and acetic anhydride. Treatment with sodium methoxide converts the lactone into *β-benzyl-α-3-bromo-4-methoxybenzylidenepropionic acid*, $OMe{\cdot}C_6H_3Br{\cdot}CH{:}C(CH_2Bz){\cdot}CO_2H$, m. p. about 155°, which is rapidly re-converted into the lactone by acids.

The action of magnesium ethyl bromide on the *cyclo*propane ester yields: (1) *methyl* 2-m-*bromo*-p-*methoxyphenyl*-3-*α*-*hydroxy*-*α*-*phenylpropyl*cyclo*propane*-1:1-*dicarboxylate*,

$$\begin{array}{l} OMe\cdot C_6H_3Br\cdot CH \\ OH\cdot CEtPh{-}{-}{-}CH \end{array}\!\!>C(CO_2Me)_2,$$

m. p. 135°, and (2) a small proportion of an isomeric *ester*, m. p. 161°.

Similarly, the action of magnesium phenyl bromide yields *methyl* 1 : 2-*dibenzoyl*-3-m-*bromo*-p-*methoxyphenyl*cyclo*propane*-1-*carboxylate*, $\begin{array}{l} OMe\cdot C_6H_3Br\cdot CH{-}{-} \\ \qquad\qquad\quad CHBz \end{array}\!\!>CBz\cdot CO_2Me$, m. p. 184°; the corresponding *acid*, $C_{25}H_{19}O_5Br$, m. p. 175°, remains undecomposed at 220°. Reduction of the ester, m. p. 184°, by means of zinc dust and acetic acid yields *methyl* *αγ*-*dibenzoyl*-*β*-3-*bromo*-4-*methoxyphenylbutyrate*, $CO_2Me\cdot CHBz\cdot CH(CH_2Bz)\cdot C_6H_3Br\cdot OMe$, m. p. 182°, the corresponding acid having m. p. 135° (decomp.).

Methyl *β*-*benzoyl*-*γ*-*phenyl*-*γ*-3-*bromo*-4-*methoxyphenylethylmalonate*, $OMe\cdot C_6H_3Br\cdot CHPh\cdot CHBz\cdot CH(CO_2Me)_2$, m. p. 176°, is obtained in small yield when the *cyclo*propane ester is treated with an excess of ice-cold magnesium phenyl bromide; oxidation of the corresponding *acid* with chromic acid gave no definite products. [3-*Bromo*-4-*methoxybenzophenone*, prepared by brominating 4-methoxybenzophenone, has m. p. 69°.]

The action of nitric acid on the *cyclo*propane ester, m. p. 153°, yields: (1) the *nitro*-substituted ester,

$$OMe\cdot C_6H_2Br(NO_2)\cdot CH\!<\!\begin{array}{l} CHBz \\ CH(CO_2Me)_2 \end{array},$$

m. p. 113°; the corresponding *methyl hydrogen* ester, $C_{20}H_{16}O_8NBr$, was also prepared; (2) a small quantity of a yellow compound, m. p. 223°. T. H. P.

The Pungent Principles of Ginger. I. A New Ketone, Zingerone [4-Hydroxy-3-methoxyphenylethyl Methyl Ketone] Occurring in Ginger. HIROSHI NOMURA (T., 1917, **111**, 769—776).—By extracting dry ginger with ether in the cold, a syrup was obtained which was extracted with sodium hydroxide and precipitated by carbon dioxide. An oil was ultimately obtained amounting to about 1 per cent. of the original ginger. From this a ketone, m. p. 40—41°, was extracted by sodium hydrogen sulphite. This ketone, *zingerone*, forms a *benzoyl* derivative, m. p. 126—127°, an acetyl derivative, b. p. 204—205°/14 mm., m. p. 40—42°, and a *methyl* derivative, b. p. 186°/16 mm., m. p. 55—56°, of which the *oxime* melts at 93—93·5°. Ethylation yields *ethylzingerone*, m. p. 66°. Methylzingerone oxidised with potassium permanganate yielded veratric acid, whilst with sodium hypochlorite, veratric acid and another acid, m. p. 95—99°, probably *β*-3:4-dimethoxyphenylpropionic acid, were obtained. With sodium hypobromite, bromoform and *β*-3:4-dimethoxyphenylpropionic acid were formed. Oxidation of ethyl

zingerone with sodium hypochlorite yielded ethylvanillic acid. These experiments indicate that zingerone is 4-hydroxy-3-methoxyphenylethyl methyl ketone, and this was corroborated by synthesis. Vanillin and acetone on condensation yield 4-hydroxy-3-methoxystyryl methyl ketone, which by reduction with hydrogen in the presence of platinum-black yielded synthetic zingerone.

T. S. PA.

The Pungent Principle of Ginger. I. The Chemical Characters and Decomposition Products of Thresh's "Gingerol," ARTHUR LAPWORTH, (MRS.) LEONORE KLETZ PEARSON, and FRANK ALBERT ROYLE (T., 1917, **111**, 777—790).—In continuation of the work of Garnett and Grier, the authors have examined the oleo-resin gingerol first investigated by Thresh. The residue from an alcoholic extract of ginger was purified by re-extraction with alcohol and with hot petroleum. The purest material thus obtained was a viscous, faintly yellow oil entirely soluble in dilute aqueous alkali. It distilled in the cathode ray vacuum from a bath at a temperature of 135—140°. The pure samples do not give a crystalline product with sodium hydrogen sulphite, but do so after distillation and other treatment. Gingerol has a phenolic character and can easily be methylated with methyl sulphate. The methylgingerol obtained melted at 64° and is optically active, $[\alpha]_D^{21}$ (chloroform, $p=2$), $+27\cdot3°$. Methylgingerol forms an oxime hydrate and appears also to contain another hydroxyl group. Oxidation of gingerol with chromic acid yielded mainly *n*-heptoic, and probably *n*-hexoic, acid, whilst methylgingerol on oxidation yielded the same mixture of fatty acids along with veratric acid. Samples of gingerol which had been distilled under diminished pressure yield, on steam distillation, some heptaldehyde, whilst from the residue sodium hydrogen sulphite extracts a ketone which can be liberated as a sweet-smelling oil with a very pungent taste. This ketone, zingerone, is most readily obtained by decomposing gingerol with hot baryta water into aldehydes, mainly volatile in steam, and the new ketone. Methylgingerol decomposes in much the same way to give methylzingerone. Zingerone is a colourless solid, m. p. 31—34°, only slightly volatile in steam. It has a phenolic character and forms a *phenylhydrazone*, m. p. about 143°, a *semicarbazone*, m. p. about 133°, and an *ethylcarbonato*-derivative, m. p. 45—47°. Methylzingerone was also prepared by methylation of zingerone with methyl sulphate, m. p. 55·5—56·2°. The methyl derivative has no phenolic properties; when oxidised with permanganate it gives veratric acid, m. p. 179°; it forms an oxime, m. p. 91—92°. Methylzingerone warmed with aqueous sodium hypobromite yielded bromoform and β-3:4-dimethoxyphenylpropionic acid, whence zingerone is probably 4-hydroxy-3-methoxyphenylethyl methyl ketone. It appears, therefore, that the oleo-resin gingerol is essentially a mixture of optically active saturated phenolic compounds derived from a residue of zingerone associated with a

molecular proportion of the residue of a saturated aliphatic aldehyde which in the main constituent is *n*-hexaldehyde.

T. S. PA.

The Pungent Principle of Ginger. II. Synthetic Preparations of Zingerone, Methylzingerone, and some Related Acids. ARTHUR LAPWORTH and FREDERICK HENRY WYKES (T., 1917, **111**, 790—798).—Methylzingerone was readily synthesised by reduction of the 3:4-dimethoxystyryl methyl ketone formed by the interaction of veratraldehyde and acetone. The corresponding synthesis of zingerone from vanillin offered difficulties, but it was found that vanillin could be readily converted into ethyl vanillylideneacetoacetate, which was reduced by means of sodium amalgam, the product with excess of alkali yielding an acid, doubtless vanillylacetoacetic acid, which when heated lost carbon dioxide and was converted into zingerone. The authors' work included syntheses of hydroferulic acid and hydrocaffeic acid. In the former case, vanillin was converted into ethyl vanillylidenemalonate or ethyl vanillylidenecyanoacetate, which was then reduced at the double bond, and on hydrolysis yielded an acid, vanillylmalonic acid, which on heating gave hydroferulic acid. A similar process with protocatechualdehyde gave hydrocaffeic acid. Hydroferulic acid is easily converted into hydrocaffeic acid by heating it with dilute hydrochloric acid at 200°. T. S. PA.

Gingerol and Paradol. E. K. NELSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1466—1469).—Some notes on the pungent principles of ginger and grains of paradise (*Amomum melegueta*). In view of Lapworth's researches (T., 1917, **111**, 777—798), the work has been discontinued. Gingerol and paradol yield the same dimethyl ether, but the latter is the more stable towards boiling 2*N*-alcoholic potassium hydroxide. They appear to be isomeric monomethyl ethers of the same dihydric phenol. J. C. W.

Preparation of α-Benzildioxime. K. VON AUWERS (*Ber.*, 1917, **50**, 952—953. Compare Grossmann and Mannheim, this vol., ii, 391).—The author points out that the process suggested by Grossmann and Mannheim for the preparation of α-benzildioxime was already described by him in 1888, and that Atack's method (A., 1913, ii, 730) is not so unsuitable as these authors suppose. J. C. W.

Synthesis of Indandiones. VI. MARTIN FREUND and KARL FLEISCHER [Sections I.—IV. with EDUARD GOFFERJÉ, V. with JOHANN STEMMER] (*Annalen*, 1917, **414**, 1—53. Compare A., 1916, i, 317, and earlier, and for nomenclature Ephraim, A., 1901, i, 688).—The synthesis of indandiones has now been extended to systems in which there is not only one five-membered ring condensed with a benzene nucleus, but two, in the two possible ways, and even three. The authors propose a new nomenclature for the series, referring to the parent hydrocarbons as benzhydrindene,

symmetrical and vicinal benzdihydrindenes, and benztrihydrindene.

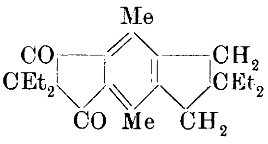
I. *A New Method for the Preparation of Benzenepentacarboxylic Acid.*—The oxidation of an alkylated indandione, if a suitable one can be found, offers a convenient method for the preparation of a benzene polycarboxylic acid, and such a synthesis is readily carried through in the case of benzenepentacarboxylic acid. *p*-Xylene is condensed with acetyl chloride to form 2:5-dimethylacetophenone, b. p. 224—225°; this is reduced by Clemmensen's method to 1:4-*dimethyl*-2-*ethylbenzene*, b. p. 185—186°, $D^{22°}$ 0·8750, n_D 1·5051, and this is condensed with diethylmalonyl chloride under the influence of aluminium chloride. The product, 4:7-*dimethyl*-2:2:5-*triethylindan*-1:3-*dione*,

$$C_6HMe_2Et{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}CEt_2,$$

is a pale yellow, viscous, aromatic oil, b. p. 183—184°/11 mm., D 1·033, which yields benzenepentacarboxylic acid, m. p. 238°, when heated with fuming nitric acid at 140° for seven hours. All the yields are good. In addition to corroborating Wolff's description of this acid (A., 1902, i, 678), the authors have prepared the *silver* salt and the *dianhydride*.

The acid has also been made, starting with 4:7-dimethyl-2:2-diethylhydrindene (*loc. cit.*), but this method is of no practical value. The hydrocarbon is condensed with acetyl chloride to form 5-*acetyl*-4:7-*dimethyl*-2:2-*diethylhydrindene*, a pale yellow oil, b. p. 150—160°/23 mm. (*semicarbazone*, m. p. 204—205°), and this is oxidised by fuming nitric acid.

II. *Higher Diethylindandione—Condensation Products of* p-*Xylene.*—When 4:7-dimethyl-2:2-diethylhydrindene and 4:7-dimethyl-2:2:5-triethylhydrindene are condensed with diethylmalonyl chloride, they yield the same product, 4:8-dimethyl-2:2:6:6-tetraethyl-*s*-benzdihydrinden-1:3-dione [4:8-dimethyl-2:2:6:6-tetraethyl-*s*-hydrindacene-1:3-dione] (annexed formula). This forms mellitic acid on oxidation, which proves it to be a hexa-substituted derivative of benzene. The synthesis and reactions of the compound form the subject of this section.



4:7-Dimethyl-2:2:5-triethylindan-1:3-dione (above) is reduced by means of amalgamated zinc and hydrochloric acid to 4:7-*dimethyl*-2:2:5-*triethylhydrindene*, a petroleum-like oil, b. p. 163—164°/14 mm., D 0·916, n_D 1·51592. 4:8-*Dimethyl*-2:2:6:6-*tetraethyl*-s-*hydrindacene*-1:3-*dione* crystallises in leaflets, m. p. 103°, and may be reduced, as above, to 4:8-*dimethyl*-2:2:6:6-*tetraethyl*-s-*hydrindacene*, which forms elongated, rhombic leaflets, m. p. 69—71°. Both compounds yield mellitic acid on heating with pure nitric acid, but the diketone forms intermediately 4:7-*dimethyl*-2:2-*diethylindan*-1:3-*dione*-5:6-*dicarboxylic acid*,

$$CEt_2{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6Me_2(CO_2H)_2,$$

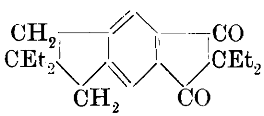
decomp. 315—320°, which shows that the reduced 5-ring is the weaker of the two in this case. When the diketone is boiled with concentrated potassium hydroxide, however, the other ring is ruptured in the usual way, the product being 6-*α-ethylbutyryl-*4 : 7-*dimethyl-*2 : 2-*diethylhydrindene-*5-*carboxylic acid*,

$$CHEt_2\cdot CO\cdot C_6Me_2(CO_2H){<}{}^{CH_2}_{CH_2}{>}CEt_2,$$

which crystallises in radiating filaments, m. p. 125°.

Attempts to prepare the 1 : 3 : 5 : 7-tetraketone corresponding with the above diketone by heating *p*-xylene with an excess of diethylmalonyl chloride in the presence of aluminium chloride were fruitless, the result merely being that a theoretical yield of 4 : 7-dimethyl-2 : 2-diethylindan-1 : 3-dione was obtained. This ketone itself could not be made to react further with diethylmalonyl chloride.

III. *Higher Diethylindandione—Condensation Products of Benzene.*—When 2 : 2-diethylindan-1 : 3-dione (from benzene and diethylmalonyl chloride) is reduced by Clemmensen's method, it forms 2 : 2-*diethylhydrindene*, as a pleasant-smelling oil, b. p. 118°/16 mm., D 0·9162, n_D^{25} 1·5135. This hydrocarbon condenses with diethylmalonyl chloride to form a mixture of 2 : 2 : 6 : 6-*tetraethyl-s-hydrindacene-*1 : 3-*dione* and 2 : 2 : 7 : 7-*tetraethyl-*as-*hydrindacene-*1 : 3-*dione*,



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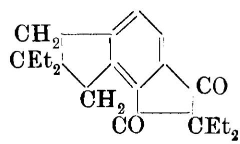
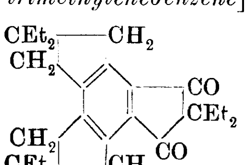


The mixture is a yellow, viscous oil, b. p. 221—238°/14 mm., which yields pyromellitic and mellophanic acids on oxidation with pure nitric acid, in the proportion of about 2 : 3. This indicates that the production of the unsymmetrical diketone is favoured. The mixture may be reduced by Clemmensen's method to the mixture of *tetraethylhydrindacenes*, m. p. 64°, b. p. 195—205°/26 mm., D^{20} 0·941, n_D 1·5182, only one of which, the unsymmetrical one, is capable of condensing with diethylmalonyl chloride to form a new indandione. This it does, and 2 : 2 : 5 : 5 : 8 : 8-*hexaethylbenztrihydrinden-*1 : 3-*dione*, [1 : 3-*diketo-*2 : 2 : 5 : 5 : 8 : 8-*hexaethyltrimethylenebenzene*] (annexed formula) may be isolated from the product, in the form of glistening, hexagonal scales, m. p. 62—63°, which yield mellitic acid on oxidation.



IV. *A New Method for the Preparation of Pyromellitic Acid.*—2-Ethyl-*p*-xylene (section I., above) is condensed with acetyl chloride to form 2 : 5-*dimethyl-*4-*ethylphenyl methyl ketone*, m. p. 30—31°, b. p. 145—147°/19 mm., D^{20} 0·9832, n_D^{20} 1·5352, which yields a *semicarbazone*, in elongated, rhombic tablets, m. p. 173—174°. The ketone yields pyromellitic acid on

oxidation with pure nitric acid, but in one experiment a small amount of the intermediate product, 2 : 5-dimethylterephthalic acid, was obtained as well. On reduction, the ketone gives 1 : 4-*dimethyl*-2 : 5-*diethylbenzene*, which is a pleasant-smelling oil, b. p. 104·5—105°/15 mm., D^{20} 0·8803, n_D 1·5091.

V. *Indandiones from Dimethylmalonyl Chloride and Fluorene.*—When fluorene is condensed with dimethylmalonyl chloride, it yields at least three crystalline derivatives, which may be separated by fractional distillation, followed by crystallisations from benzene and alcohol. One of them is an iso*butyrylfluorene* (*fluorenyl* iso*propyl ketone*), $CH_2<\begin{matrix}C_6H_3\cdot CO\cdot CHMe_2\\ | \\ C_6H_4\end{matrix}$, m. p. 80—82°, the production of which is due to the rearrangement of the acyl chloride into *iso*butyryl chloride. The others are two of the three possible dimethylindandiones, but it is impossible to say which they are, as no polycarboxylic acids could be obtained on oxidation. *α-Fluorenedimethylindandione* [(*α*)-1 : 3-*Diketo*-o-*benzylene*-2 : 2-*dimethylhydrindene*], m. p. 220—221°, is sparingly soluble in alcohol; the *β-compound*, m. p. 156—158°, is freely soluble in the hot liquid. The mixture of the three ketones may be reduced by Clemmensen's method, and the products are more easy to separate. iso*Butylfluorene* has m. p. 68—70°; *α-fluorenedimethylhydrindene* [(*α*)-o-*benzylene*-2 : 2-*dimethylhydrindene*] has m. p. 128—129°, and the *β-isomeride* has m. p. 135—137°. The two indandiones yield *fluorenonedimethylindandiones* [1 : 3-*diketo*-o-*benzoylene*-2 : 2-*dimethylhydrindenes*], $\begin{matrix}C_6H_4\\ | \\ CO\text{--}\end{matrix}>C_6H_2<\begin{matrix}CO\\ CO\end{matrix}>CMe_2$, on oxidation with sodium dichromate and acetic acid; both *α*- and *β*-compounds have m. p. 263°, but the mixture melts at about 30° lower. The *β*-compound suffers hydrolysis and rupture of the typical benzylene ring on boiling with sodium hydroxide, the product being an *acid*, m. p. 237—238°, of the formula

$$CO_2H\cdot C_6H_2Ph<\begin{matrix}CO\\ CO\end{matrix}>CMe_2 \quad \text{or} \quad CO_2H\cdot C_6H_4\cdot C_6H_3<\begin{matrix}CO\\ CO\end{matrix}>CMe_2.$$

J. C. W.

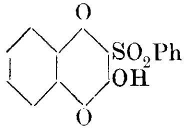
Dihydroxydiarylsulphones. O. HINSBERG (*Ber.*, 1917, **50**, 953—958).—It has already been shown that aromatic sulphinic acids combine with *o*- and *p*-quinones and quinone-imines, provided that these contain no acidic or basic substituents, to form sulphones (A., 1895, i, 144, 471; 1896, i, 684). Further applications of this reaction are now described.

Anthraquinone-2-sulphinic acid and benzoquinone yield 2 : 5-*dihydroxyphenyl*-2′-*anthraquinonylsulphone*,

$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4\cdot SO_2\cdot C_6H_3(OH)_2,$$

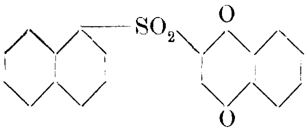
in yellow scales, m. p. 220°, which dissolve in sodium hydroxide with a green colour. Benzenesulphinic acid and 1 : 4-naphtha-

quinone form 1 : 4-*dihydroxy-2-naphthylphenylsulphone*, which separates in colourless crystals, m. p. 178°, and is oxidised by alkaline potassium ferricyanide to 3-*hydroxy-2(1 : 4)-naphthaquinonylphenylsulphone* (annexed formula), yellowish-green prisms, m. p. 214°. *p*-Benzoquinone and β-naphthalenesulphinic acid yield 2 : 5-*dihydroxyphenyl-2'-naphthylsulphone*, prisms, m. p. 216°, whilst α-naphthaquinone gives 1 : 4-*dihydroxy-2 : 2'-dinaphthylsulphone*,



$$C_{10}H_7 \cdot SO_2 \cdot C_{10}H_5(OH)_2,$$

leaflets, m. p. 174°. 2 : 5-*Dihydroxyphenyl-1'-naphthylsulphone* has m. p. 208°, and forms a *dimethyl ether*, m. p. 205°; 1 : 4-*dihydroxy-2 : 1'-dinaphthylsulphone* has m. p. 191°, yields a *diacetate*, m. p. 222°, and is oxidised by chromic acid to 2(1 : 4)-*naphthaquinonyl-1'-naphthylsulphone* (annexed formula), yellow prisms, m. p. 227°. β-Naphthaquinone and α-naphthalenesulphinic acid yield 3 : 4-*dihydroxy-1 : 1'-dinaphthylsulphone*, m. p. 199°.



J. C. W.

Crystallisation of Menthol. FRED. E. WRIGHT (*J. Amer. Chem. Soc.*, 1917, **39**, 1515—1524).—Menthol crystallises in at least four different forms, of which only the α-form is stable between 0° and its m. p., 42·5°. The other three forms are monotropic, and melt respectively at 35·5° (β), 33·5° (γ), and 31·5° (δ). On account of the readiness with which the liquid may be undercooled, the three monotropic forms are easily obtained. The temperature of crystallisation appears to be the chief factor which determines the nature of the solid product. The unstable modifications are transformed into the α-form on keeping, but in this process the δ-modification may first pass into the β-form. All the forms of menthol show a pronounced tendency towards the development of radial spherulites. These are approximately spherical when the crystals are formed from the liquid fusion, but noticeably ellipsoidal when the α-crystals result from the transformation of the monotropic modifications. H. M. D.

Volatile Constituents of Leaves of Alpina nutans, Roscoe. K. KAFUKU, *Kogyo-Kwagaku-Zasshi* (*J. Chem. Ind. Tokyo*, 1917, **20**, 349—353; from *J. Soc. Chem. Ind.*, 1917, **36**, 905).—The leaves of *Alpina nutans*, Roscoe, contain 0·053% of a volatile oil, D^{19} 0·9301, n_D^{20} 1·4750, α_D (100 mm.) +38·4°; saponification value, 9·88; saponification value after acetylation, 36·1. The chief constituents of the oil are *d*-camphor (more than 30%) and *d*-camphane (17%). Other constituents are cineol and an ester of cinnamic acid, and probably limonene, a sesquiterpene, and a phenol of high boiling point. T. S. P.

Optical Activity of Pine Species. D. E. TSAKALOTOS (*Gazzetta*, 1917, **47**, i, 285—287).—Oil of turpentine from *Pinus halepensis* (Aleppo pine) has $[\alpha]_D$ +47—48°, whereas that from *P. maritima* has $[\alpha]_D$ −40·5°. Gildemeister's statement ("Die aetherischen Oele," Leipzig, 1913, II, 133) that Belloni obtained Aleppo pine-needle oils with $[\alpha]_D$ −22·355° and −26·518°, is erroneous, these oils being obtained from *P. maritima*. Genuine Aleppo pine-needle oil consists largely of *d*-pinene, independently of the locality or of the season when it is distilled; a sample from Attica was found to have $[\alpha]_D$ +39·4°. T. H. P.

Products of Oxidation of Aloin. E. SEEL, C. KELBER, and W. SCHARF (*Ber.*, 1917, **50**, 759—764).—By the oxidation of aloin in aqueous solution with Caro's acid, the authors have obtained a trihydroxymethylanthraquinone ("aloe-emodin," compare Seel, A., 1901, i, 92; *Süddeutsch. Apothekerzeitung*, 1906, 624), together with a red, crystalline *tetrahydroxymethylanthraquinone*, m. p. 193—195° (*tetra-acetyl* derivative, yellow, crystalline powder, m. p. 198—201°; *tetrabenzoyl* derivative, yellow, crystalline powder, m. p. 236—238°). The same tetrahydroxy-compound was formed in the oxidation of aloin with aqueous hydrogen peroxide. Hydrolysis of the acetyl and benzoyl derivatives gave rise to a substance of the composition of a tetrahydroxymethylanthraquinone, but of m. p. 232—234°. D. F. T.

Bixin. J. HERZIG and F. FALTIS (*Ber.*, 1917, **50**, 927—929. Compare Heiduschka and Panzer, this vol., i, 408).—It is claimed that the real difficulty in determining the empirical formula of bixin lies in the fact that the combustion of the pigment requires special precautions. By observing these, results agreeing with $C_{26}H_{30}O_4$ are always obtained. J. C. W.

Uroerythrin. V. BORRIEN (*J. Pharm. Chim.*, 1917, [vii], **16**, 45—51).—Uroerythrin may be readily obtained in alcoholic solution from urine by shaking it with powdered talc, collecting the sediment, washing it well with water, and extracting the solid residue with 95% alcohol alone or slightly acidified with hydrochloric acid. The brick-red sediments from certain urines also yield this pigment in a purer state if they are mixed with talc, washed with water, and extracted as above. Such alcoholic solutions, when exposed to light, rapidly lose their colour, the pigment being destroyed. From an alcoholic solution, kept in the dark, there is a slow deposition of the pigment on the walls of the containing vessel. The absorption spectrum of its alcoholic solution shows two bands, one at λ=550—525, and the other at λ= 510—484. An alcoholic solution of uroerythrin gives with a few drops of dilute solutions of ammonium, sodium, or potassium hydroxide a greenish-blue coloration. Dilute acids give a pink coloration. The pigment probably exists in the urine in a colloidal state and its abundance is proportional to the amount of uric acid or urates contained in the urine. W. G.

The Mass Action of Water on Dyes. William M. Dehn (*J. Amer. Chem. Soc.*, 1917, **39**, 1338—1348).—A large number of dyes are found to undergo colour changes on diluting largely with water. Sensitive solutions of this nature are obtained in some cases when the dye is mixed with only a trace of acid or alkali, but other dyes require relatively large quantities of acid or alkali to make sensitive solutions. Starting with an acid solution, if the colour has been changed by dilution, the addition of acid will restore the original shade, and similarly, alkalis will restore the colour of a changed alkaline dye. For example, a red, feebly alkaline solution of cochineal becomes blue on dilution, and red again on adding alkali; a fairly acid solution of methyl-violet changes from greenish-orange to green, blue, indigo, and finally violet; strongly alkaline solutions of picric acid change from red to yellow. A table showing the behaviour of some sixty-three dyes is given, but at least one hundred other dyes were found to be unaffected by dilution.

The common indicators suffer changes in colour by dilution only when the amount of acid or alkali present is very small. The most serviceable indicator is therefore one that is stable towards water in the presence of the smallest concentration of OH or H ions. No dyes give sensitive solutions in both alkaline and acidic media, and altogether it may be assumed that the effects are not due to ionisation, but to the mass action of the water in causing chromoisomerisation or some other change of the molecule.

The colours of the above dyes in pyrophosphoric acid solutions are also recorded. Basic dyes are found to be prevailingly red in pyrophosphoric acid, although many of them have other shades in concentrated aqueous solutions. In fact, it is more than probable that the colour exhibited in an aqueous solution is really that of the mixture of products formed by hydrolytic action. If the phosphoric acid solutions are diluted with water, the colour changes are in the order of the spectrum.

The mechanism of the hydrolysis of dyes is briefly discussed. As is generally recognised, the changes in molecular state which a dye may undergo may be due to (1) different colloidal forms, (2) polymerisation, (3) quinhydrone formation, (4) hydration, or (5) tautomerism, in all of which water may be operative. J. C. W.

Pyrylium Compounds. II. Walther Dilthey (*J. pr. Chem.*, 1917, [ii], **95**, 107—120. Compare A., 1916, i, 829).—Triphenylpyranol, the synthesis of which was described in the earlier paper, is an amphoteric substance capable of giving coloured salts with acids and also with alkalis, although the products of the latter class, which form yellowish-red solutions, are unstable and readily undergo fission with formation of benzoic acid and an unidentified oily compound The presence of the hydroxyl group in triphenylpyranol can be proved by treatment with methyl iodide and sodium methoxide in methyl-alcoholic solution with formation of 2-*methoxy*-2 : 4 : 6-*triphenylpyran*, $CH{<}{\substack{CPh\text{---}O\\CPh{:}CH}}{>}CPh{\cdot}OMe$,

tablets or prisms, m. p. 142—143° (corr.), insoluble in alcoholic potassium hydroxide. All other attempts to demonstrate the presence of the hydroxyl group proved fruitless, the pyranol compound in some cases proving refractory and in other cases undergoing decomposition. With hydrazine hydrate in pyridine solution, colourless needles, m. p. 123—125° (decomp.), were obtained of a *substance* (deep brown *picrate*, m. p. 166°, corr.), of which the constitutional formula probably is $CPh{<}{\begin{smallmatrix}CH\equiv\equiv CPh\\ CH\cdot CPh(OH)\end{smallmatrix}}{>}N\cdot NH_2$; this substance, unlike triphenylpyranol, failed to react with semicarbazide, and when heated above its m. p. gave rise to 2:4:6-triphenylpyridine. In the earlier publication the action of semicarbazide on triphenylpyranol has been shown to yield $\alpha\gamma\epsilon$-triphenyl-Δ^{β}-penten-$\alpha\epsilon$-dione disemicarbazone; the interaction of benzylidenediacetophenone and semicarbazide in pyridine solution forms a quite distinct substance, namely, the *disemicarbazone*, $CHPh(CH_2\cdot CPh{:}N\cdot NH\cdot CO\cdot NH_2)_2$, prisms, m. p. 232—233° (corr.).

For the synthesis of the trianisylpyrylium complex, it was not possible to follow exactly the method employed for triphenylpyranol, and it was found necessary first to effect the condensation of anisaldehyde and *p*-methoxyacetophenone in the presence of alkali to the corresponding oily diketone, which, without being purified, was then heated with ferric chloride, acetic acid, and acetic anhydride. The resulting 2 : 4 : 6-*trianisylpyryl ferrichloride*, $OMe\cdot C_6H_4\cdot C{<}{\begin{smallmatrix}CH{:}C(C_6H_4\cdot OMe)\\ CH\cdot C(C_6H_4\cdot OMe)\end{smallmatrix}}{\geqslant}OCl,FeCl_3$, brownish-yellow needles, m. p. 271—272° (corr.), which in acetic acid, alcohol, or pyridine gives solutions with a greenish-yellow fluorescence, yields its pseudo-base on treatment with sodium carbonate solution, sodium acetate failing to produce this result. The pseudo-base in this case is not the simple pyranol compound, but its dehydration product, 2:4:6-*trianisylpyran oxide*,

$$O\left[C(C_6H_4\cdot OMe){<}{\begin{smallmatrix}O\text{---}C(C_6H_4\cdot OMe)\\ CH{:}C(C_6H_4\cdot OMe)\end{smallmatrix}}{>}CH\right]_2,$$

colourless needles, m. p. 84° (corr.), soluble in sulphuric acid with a greenish-yellow fluorescence; this, in ethereal solution with picric acid, formed red 2:4:6-*trianisylpyryl picrate*, m. p. 278—279° (corr.), dilute solutions of which exhibit a beautiful fluorescence.

4-*Phenyl*-2 : 6-*dianisylpyryl ferrichloride*,

$$CPh{<}{\begin{smallmatrix}CH{:}C(C_6H_4\cdot OMe)\\ CH\cdot C(C_6H_4\cdot OMe)\end{smallmatrix}}{\geqslant}OCl,FeCl_3,$$

prepared like the triphenylpyryl analogue by the interaction of *p*-methoxyacetophenone (2 mols.), benzaldehyde (1 mol.), and ferric chloride in hot acetic anhydride, forms brownish-red prisms, m. p. 265—266° (corr.), with a green glance, and gives solutions with a yellow fluorescence; on treatment with sodium carbonate, the ferrichloride yielded 4-*phenyl*-2 : 6-*dianisylpyranol*,

$$CH{<}{\begin{smallmatrix}C(C_6H_4\cdot OMe)\cdot O\\ CPh\equiv\equiv CH\end{smallmatrix}}{>}C(C_6H_4\cdot OMe)\cdot OH,$$

almost colourless needles, m. p. 106°, which gives a strongly

fluorescent solution in sulphuric acid, and in ethereal solution reacts with picric acid, forming 4-*phenyl*-2 : 6-*dianisylpyryl picrate*, red needles, m. p. 272—273° (corr.). D. F. T.

The Crystalline Form of Maltol (Lariscinic Acid, 3-Hydroxy-2-methyl-1 : 4-pyrone). H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1916, **55**, 377—379).—Maltol exists in two modifications, an α-monoclinic and a β-rhombic form. By crystallisation from chloroform the α-variety alone is obtained, generally in the form of small, thin tables [$a:b:c = 0·3977:1:0·4013$; $\beta = 109°40'$]. From 50% alcohol solution the α- and β-forms are obtained together. The rhombic crystals of the latter have [$a:b:c = 0·5490:1:0·5867$]. From the fact that, if crystals of the β-form are placed in a saturated chloroform solution they disappear and give place to the α-form, it is concluded that the α-form is the stable modification. E. H. R.

The Hydrolysis of Chromones by Dilute Alkali. H. SIMONIS (*Ber.*, 1917, **50**, 779—786).—The fission of the heterocyclic ring in the chromones by an approximately *N*-aqueous solution of sodium hydroxide occurs generally at the ether–oxygen atom, the primary product of the typical constitution

$$OH·C_6H_4·CO·CHR·COR$$

undergoing further decomposition, so that the final product is the corresponding salicylic acid derivative.

In the case of 2 : 3 : 5-trimethylchromone, it has already been observed that the action of alkali yielded an oily product without acidic character (Simonis and Lehmann, A., 1914, i, 424), and the assumption that this product was 2-hydroxy-6-tolyl ethyl ketone, $OH·C_6H_4Me·COEt$, is now confirmed, the substance having been obtained in a pure, crystalline condition, prisms, m. p. 28·5°. The abnormal course of the fission process with this substance is probably due to the influence of the methyl radicle in the 5-position, because the 2 : 3 : 6- and 2 : 3 : 8-trimethylchromones yield the corresponding salicylic acids, whilst 2 : 3 : 5 : 7-tetramethylchromone and 5-bromodimethylchromone give rise respectively to 5-*hydroxy*-4-m-*xylyl ethyl ketone*, $OH·C_6H_3Me_2·COEt$, colourless needles, m. p. 78°, and 6-*bromo*-2-*hydroxyphenyl ethyl ketone*, $OH·C_6H_3Br·COEt$, colourless prisms, m. p. 82°, although 7-bromodimethylchromone under similar conditions forms 4-*bromosalicylic acid*,

$$OH·C_6H_3Br·CO_2H,$$

colourless needles, m. p. 212°; likewise, in the hydrolytic fission of 2 : 3 : 5 : 8-tetramethylchromone, no dimethylsalicylic acid is produced. The effect of a substituent in the 5-position therefore appears to be a general one. D. F. T.

2 : 3 : 5 : 7-Tetramethylchromone. H. SIMONIS and L. HEROVICI (*Ber.*, 1917, **50**, 787—793. Compare Simonis, preceding abstract).—2 : 3 : 5 : 7 - Tetramethylchromone, $C_6H_2Me_2{<}\begin{matrix}CO·CMe\\ \| \\ O—CMe\end{matrix}$, needles, m. p. 100·5°, was obtained by the action of phosphoric

oxide on a mixture of methyl methylacetoacetate and *s*-xylenol containing a little alcohol. The chromone forms a *hydrochloride*, m. p. 106°; *hydrobromide*, m. p. 193°; *dibromide*, $C_{13}H_{14}O_2Br_2$, m. p. 182°; *oxime*, needles or hexagonal crystals, m. p. 196°; *mercurichloride*, $C_{13}H_{14}O_2,HgCl_2$, needles, m. p. 202—203°; *mercurichloride-hydrochloride*, $(C_{13}H_{14}O_2)_2,HgCl_2,HCl,H_2O$, colourless crystals; *uranyl chloride-hydrochloride*, $(C_{13}H_{14}O_2)_2,UO_2Cl_2,2HCl$, yellow solid; *additive* compound with gold chloride,

$$(C_{13}H_{14}O_2)_2,AuCl_3,$$

orange-yellow solid, m. p. 176°; *platinichloride*,

$$(C_{13}H_{14}O_2)_2,H_2PtCl_6,$$

reddish-yellow solid, m. p. 202°; *ferrichloride-hydrochloride*, $(C_{13}H_{14}O_2)_3,FeCl_3,2HCl$, yellow, crystalline solid, m. p. 150—152°; *additive* compound with potassium iodide and iodine,

$$(C_{13}H_{14}O_2)_3,KI,I_3,$$

bronzy needles, m. p. 79—81°.

By nitration in the cold with a mixture of sulphuric and fuming nitric acids, 6-*nitrotetramethylchromone*, $NO_2\cdot C_6HMe_2<\begin{matrix}CO\cdot CMe\\ \|\\ O{-}{-}CMe\end{matrix}$, colourless needles, m. p. 128—129°, was obtained, whilst treatment at 110° with phosphorus pentasulphide produced 2:3:5:7-tetramethyl-4-thiochromone, $C_6H_2Me_2<\begin{matrix}CS\cdot CMe\\ \|\\ O{-}{-}CMe\end{matrix}$. D. F. T.

Decomposition of Quinine Hydrogen Sulphate. B. F. Howard and O. Chick (*Pharm. J.*, 1917, **99**, 143—144).—The conditions have been ascertained under which quinine hydrogen sulphate is converted into quinicine and quinotoxin. The material containing $7H_2O$ decomposes to the extent of 0·25% at 60°, whilst, if previously dried at 35—40°, no decomposition occurs at this temperature. The addition of small quantities of water (for example, half its weight) at any dangerous temperature increases the decomposition, whilst larger quantities of water retard it. The limiting temperature at which quinine hydrogen sulphate, heated alone or in very concentrated solution, first decomposes is 60°. At 90°, 50% decomposes in twenty-four hours and 75% in forty-eight hours. In an open vessel the decomposition is only 17% in twenty-four hours owing to exsiccation. Melting the hydrated salt probably always causes decomposition. The formation of a bright yellow fusion giving a highly coloured, very refractive solution, is a certain indication of decomposition. The authors suggest the use of the dihydrochloride or the dihydrobromide for solutions which require sterilisation by heat. H. W.

A Synthesis of Tropinone. Robert Robinson (T., 1917, **111**, 762—768).—The formula for tropinone suggests that the substance might, theoretically, be hydrolysed into succindialdehyde, methylamine, and acetone, and it has, in fact, been found possible to synthesise it by the interaction of these com-

pounds. The synthesis was also carried out by using ethyl acetonedicarboxylate or calcium acetonedicarboxylate instead of acetone. In the last case, the succindialdehyde was mixed in water with acetonedicarboxylic acid, which was then neutralised by the addition of calcium carbonate, methylamine, in water, being afterwards gradually added, and the mixture allowed to remain at the ordinary temperature for fifty hours. On working the product up, tropinone, melting at 42°, was obtained in a yield of 42% of the theoretical. In these experiments, the dipiperonylidene derivative was used as a means of detecting the merest traces of tropinone. This substance is readily obtained by the condensation of tropinone with piperonal in alcoholic potassium hydroxide solution, and after crystallisation from ethyl acetate forms bright yellow needles melting at 214°, which are but sparingly soluble in most organic solvents. T. S. PA.

Yohimbine and Quebrachine. EDUARDO FILIPPI (*Arch. Farmacol. sperim.*, 1917, **23**, 107—128, 129—140; from *Chem. Zentr.*, 1917, i, 1019—1020).—From purely chemical evidence, Fourneau and Page (A., 1914, i, 862) have come to the conclusion that yohimbine and quebrachine are identical. [Contrast, however, Spiegel (A., 1916, i, 287).] The author has carried out a careful pharmacological comparison of the two alkaloids, from which he is drawn to the conclusion that although they are similar in many respects, yet in others they show such marked differences that they cannot be considered as identical, although belonging to the same pharmacological group.

The chemical similarity of the two alkaloids with each other and with strychnine is further shown by the occurrence of Vitali's reaction. H. W.

Silver Compound of the Acridine Series (Disinfectant), and a Process of Making Same. SOC. CHEM. IND. BASLE (U.S. Pat., 1227624, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 905).—Compounds of value as disinfectants are obtained by the action of a soluble silver salt, in presence of a solvent, on acridine dyes which may be alkylated at the acridine nitrogen. Special claim is made for the silver compound of 3:6-diamino-2:7-dimethylacridine, methylated at the acridine nitrogen. It is a brownish-red powder, forming coloured solutions in water, alcohol, acetone, ethyl acetate, acetic acid, and sulphuric acid. It acts as a disinfectant in solutions of great dilution, strongly checking the growth of bacteria, especially streptococci and splenitis bacilli.
T. S. P.

Cadmium Compounds of the Acridine Series, and a Process of Making the Same. SOC. CHEM. IND. BASLE (U.S. Pat., 1228926, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 867).—An acridine dye, alkylated at the acridine nitrogen, is heated with a soluble cadmium salt in presence of a solvent. The cadmium

compound of 3:6-diamino-2:7-dimethylacridine, methylated at the acridine nitrogen, is specially claimed. T. S. P.

Unsymmetrical Derivatives of Aromatic Diamines. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1447—1465).—Derivatives of *m*- and *p*-phenylenediamines and 2:4-tolylenediamine are described. The chief contribution by the authors is a number of chloroacetyl derivatives (compare this vol., i, 552), but new details and improved methods of preparation are recorded in the case of several older compounds.

I. DERIVATIVES OF *m*-PHENYLENEDIAMINE.—*m*-Aminoacetanilide has m. p. 86·5—87·5° (corr.), and the hydrochloride forms transparent plates, m. p. 280°; m-*chloroacetylaminoacetanilide* crystallises in radiating masses of needles, m. p. 212—214° (decomp.). *m*-Acetylaminophenylcarbamide forms colourless aggregates of thin plates, m. p. 204—205·5° (decomp.); its hydrochloride is a feathery solid, m. p. above 275° (decomp.); m-*aminophenylcarbamide* crystallises in radiating groups of long, prismatic needles, m. p. 128—130° (corr.); m-*chloroacetylaminophenylcarbamide* forms delicate, matted needles, m. p. 192—193° (gas evolution). *m*-Aminophenylglycine (mentioned in D.R.-P., 96857) crystallises in pale brown wedges, m. p. 193—194° (decomp.); its *methyl ester dihydrochloride* (*methyl* m-*aminoanilinoacetate dihydrochloride*) forms rosettes of minute spears, decomp. 196—197°; m-*amino-anilinoacetamide*, $NH_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, crystallises in rosettes of flat needles, m. p. 145·5—146·5° (corr.).

m-Amino-oxanilic acid may be prepared by heating *m*-phenylenediamine with crystalline oxalic acid at 115—140°; it crystallises in masses of needles with $1H_2O$, m. p. 245° (decomp.), but cannot be converted into the amide. Ethyl *m*-nitro-oxanilate (from *m*-nitroaniline and ethyl oxalate at 160°) can be converted, however, into m-*nitro-oxanilamide*, m. p. 268—269° (effervescence), and this reduced by the ferrous sulphate and ammonia method to m-*amino-oxanilamide*, $NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2$, thin, hexagonal plates, m. p. 191—191·5°. m-*Chloroacetylamino-oxanilamide* forms masses of minute needles, decomp. 281°; m-*carbamido-oxanilamide* separates in voluminous, hair-like masses, decomp. above 260°; m-*chloroacetylcarbamido-oxanilamide*,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2,$$

crystallises in rosettes of flat needles and platelets, decomp. 233—234°.

Ethyl m-*nitromalonanilate*, from *m*-nitroaniline and ethyl malonate at 200—210°, crystallises in delicate, cream-coloured needles, m. p. 73·5—74°; m-*nitromalonanilide* has m. p. 198—200° (corr.); m-*aminomalonanilide*, $CH_2(CO\cdot NH\cdot C_6H_4\cdot NH_2)_2$, forms glistening, creamy needles, m. p. 180·5° (corr.).

II. DERIVATIVES OF *p*-PHENYLENEDIAMINE.—p-*Chloroacetylamino-acetanilide* forms minute prisms, decomp. 265—270°. *p*-Acetylaminophenylcarbamide yields *chloroacetyl*-p-*acetylaminophenyl*-

carbamide, $NHAc\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot CO\cdot CH_2Cl$, in lenticular platelets, m. p. 235—237° (decomp.). *p*-Aminophenylcarbamide forms flat, glistening needles or long platelets, and melts at 162—164° with evolution of gas, then resolidifies and remains solid at 285°; p-*chloroacetylaminophenylcarbamide* crystallises in aggregates of flat needles, m. p. 225° (evolution of gas; resolidification).

p-Aminoacetanilide, when boiled with sodium chloroacetate solution, yields p-*acetylaminophenyldiglycine*,

$$NHAc\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2,$$

in sheaves of needles, m. p. 234—235° (effervescence), whilst with ethyl chloroacetate it gives *ethyl* p-*acetylaminophenylglycine* (*ethyl* p-*acetylaminoanilinoacetate*), in rosettes of long, slender needles, m. p. 124—125° (corr.). This ester is hydrolysed by boiling hydrochloric acid to *p*-aminophenylglycine, m. p. 222—223° (decomp.) (compare D.R.-P., 88433); the ester dihydrochloride of this (*ethyl* p-*aminoanilinoacetate dihydrochloride*) has m. p. 201—202° (decomp.), and yields p-*aminophenylglycinamide* (p-*aminoanilinoacetamide*), m. p. 161—164°, when treated with aqueous ammonia.

p-Amino-oxanilic acid yields p-*chloroacetylamino-oxanilic acid*, as a mass of microscopic needles, decomp. 235°. *Methyl* p-*amino-oxanilate* crystallises in greenish-yellow, silky needles, m. p. 129—130° (corr.), and forms a *hydrochloride*, long, thin, pale purple plates, from which p-*amino-oxanilamide*,

$$NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2,$$

a pale purple, microcrystalline powder, m. p. 217—218°, may be prepared, and converted into p-*chloroacetylamino-oxanilamide*, which is not molten at 280°.

p-*Nitromalonanilide* forms flat, brownish-yellow needles, m. p. 241—242° (decomp.); *ethyl* p-*nitromalonanilate* crystallises in pale yellow, slender needles or platelets, m. p. 92—95°; p-*nitromalonanilamide* forms yellow, rhombic platelets, m. p. 218—220° (decomp.); p-*aminomalonanilamide* crystallises with $1H_2O$, and melts partly at 200—210°; p-*chloroacetylaminomalonanilamide*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, forms sheaves of slender filaments, m. p. 243—244° (decomp.).

III. Derivatives of 2:4-Tolylenediamine.—4-Acetylamino-*o*-toluidine hydrochloride, decomp. 263—264°, yields 4-*acetylamino*-2-*chloroacetylaminotoluene* [2-*chloroacetylaminoaceto*-p-*toluidide*] in felted masses, m. p. 230—231° (decomp.). 5-*Acetylamino*-2-*methylphenylcarbamide* [4-*acetylamino*-o-*tolylcarbamide*] crystallises in felted needles, m. p. 240° (effervescence; resolidification), and is hydrolysed by means of hydrochloric acid to 4-*amino*-o-*tolylcarbamide*, which forms stellate groups of spikes, m. p. 199—200°, and yields a *hydrochloride*, sheaves of minute needles, and also 4-*chloroacetylamino*-o-*tolylcarbamide*,

$$CH_2Cl\cdot CO\cdot NH\cdot C_6H_3Me\cdot NH\cdot CO\cdot NH_2,$$

radiating masses of delicate needles, m. p. 224—225° (evolution of gas).

J. C. W.

Pyrimidines. LXXXIV. Transformation by Hydrolysis of Secondary Pyrimidine Nucleosides into Iminazole Combinations. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1715—1717).—The crystalline compound, $C_5H_8ON_2$, obtained by hydrolysing the ethyl ether of the secondary alcohol derivative of uracil,

$$NH<\begin{matrix}CO-CH\\CO\cdot NH\end{matrix}>C\cdot CHMe\cdot OEt,$$

by means of aqueous hydrobromic acid (compare Johnson and Hadley, A., 1916, i, 754), is now found to be identical with 4:5-dimethylglyoxalone (compare Biltz, A., 1908, i, 56); its diacetyl compound was prepared. T. H. P.

Ring Formation with the Elimination of a Nitro-group. S. REICH and (MLLE.) B. TURKUS (*Bull. Soc. chim.*, 1917, [iv], **21**, 107—111).—6-Chloro- and 6-bromo-2-nitrobenzaldehydephenylhydrazone, like the corresponding 2:6-dinitro-compound (compare A., 1913, i, 995), when warmed with alcoholic potassium hydroxide lose their nitro-group and yield *iso*indazoles.

6-Bromo-2-nitrotoluene when heated in a sealed tube at 140° for six hours with bromine and magnesium carbonate yields 6-*bromo-2-nitrobenzyl bromide*, $NO_2\cdot C_6H_3Br\cdot CH_2Br$, colourless needles, m. p. 71—72°, which when warmed in alcoholic solution with aniline gives 6-*bromo-2-nitrobenzylaniline*, red crystals, m. p. 105°. This compound, when oxidised in acetone solution with potassium permanganate, yields 6-*bromo-2-nitrobenzylideneaniline*, an oil which on hydrolysis gives 6-*bromo-2-nitrobenzaldehyde*, m. p. 82°. This aldehyde gives a *phenylhydrazone*, occurring in two forms, (1) red needles, m. p. 146°, (2) yellow needles, m. p. 142°, which are readily converted the one into the other. This hydrazone when warmed with alcoholic potassium hydroxide on a water-bath gives 4-*bromo*-1-*phenyl*iso*indazole*, $C_6H_3Br<\begin{matrix}-CH\\NPh\end{matrix}>N$, pale yellow crystals, m. p. 98°. Similarly, 6-*bromo-2-nitrobenzaldehyde-β-naphthylhydrazone*, m. p. 192°, gives 4-*bromo*-1-*β-naphthyl*iso-*indazole*, m. p. 135°.

6-*Chloro-2-nitrobenzaldehydephenylhydrazone* forms red needles, m. p. 161°, and gives 4-*chloro*-1-*phenyl*iso*indazole*, m. p. 84°.

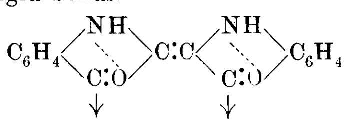
6-*Chloro-2-nitrobenzaldehyde-β-naphthylhydrazone* yields yellow needles, m. p. 178°, and gives 4-*chloro*-1-*β-naphthyl*iso*indazole*, yellow needles, m. p. 112°. W. G.

Ring Formation with the Elimination of a Nitro-group. S. REICH (*Bull. Soc. chim.*, 1917, [iv], **21**, 111—114. Compare preceding abstract).—2 : 4-Dinitrobenzaldehydephenylhydrazone, unlike its 2:6-isomeride (compare A., 1913, i, 995), does not undergo ring formation in the presence of potassium hydroxide. The influence in these cases is probably steric, since ethyl 2:4-dinitrophenylglyoxylate phenylhydrazone yields the corresponding *iso*-indazole. This view is supported by the fact that 2:4-dinitro-

acetophenonephenylhydrazone readily undergoes ring formation and 2 : 4 : 6-trinitrobenzaldehydephenylhydrazone readily yields 5 : 7-*dinitro*-1-*phenyl*iso*indazole*, red needles, m. p. 148°. W. G.

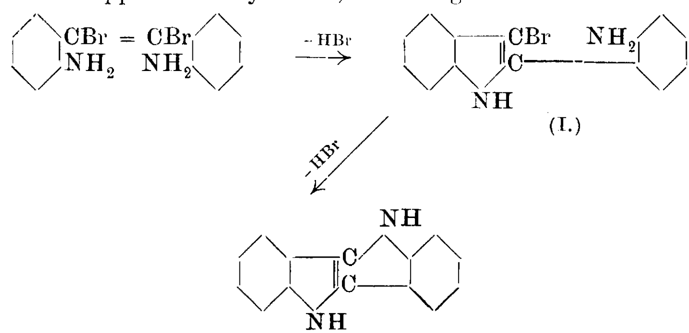
The Indigo Chromophore. I. LIFSCHITZ and HEINRICH LOURIÉ (*Ber.*, 1917, **50**, 897—906).—The absorption spectra of indigotin, "dithioindigo," and Claasz's compounds, "monosulphurylindigo" ["sulphurylindoxyl-α-indolindigo," A., 1916, i, 753] and "disulphurylindigo" ["sulphurylindigo," *ibid.*, 842], have been determined, in suitable organic solvents and in concentrated sulphuric acid. The usual curves are reproduced.

Attention is directed to the phenomenon of halochromism in the indigo series. Indigotin itself gives an olive-green solution in sulphuric acid and a bluish-green in a mixture of chloroform and stannic chloride; "dithioindigo" is emerald-green in sulphuric acid and violet in the foregoing mixture, and the whole alteration of the absorption spectra in sulphuric acid resembles that suffered by halochromic αβ-unsaturated ketones. The peculiar feature of the true indigoid chromophore is the intimate connexion between the carbonyl group and the imino-group (or sulphur atom), as Claasz has rightly emphasised (*ibid.*, 841). For ordinary chemical purposes, the authors are in agreement with Claasz's formulæ, but in optical considerations they prefer one with residual affinities, as below, in order to explain the halochromism, rather than a formula with rigid bonds.



J. C. W.

Formation of a Doubly Condensed Indole. PAUL RUGGLI (*Ber.*, 1917, **50**, 883—893).—The author describes a double application of Lipp's indole synthesis, according to the scheme:



(I.)

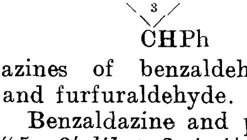
(II.)

A contraction of di-indole, namely, "dindole," is proposed as a name for the compound II. Systems of this type are known in the pyrrole series, but not in the indole group.

$\alpha\alpha$-Dibromo-2 : 2′-dinitrostilbene (Pfeiffer, A., 1912, i, 619) is reduced by means of stannous chloride dissolved in a solution of hydrogen chloride in glacial acetic acid to *$\alpha\alpha$-dibromo-2 : 2′-diaminostilbene*, which forms colourless leaflets, and suffers brisk decomposition at 168—169° when quickly heated, but undergoes rearrangement at about 125—140°, when slowly heated, into a compound with m. p. 260°. One molecule of hydrogen bromide is readily removed from this by boiling for a short time with alcoholic picric acid. *3-Bromo-2-o-aminophenylindole* (I) crystallises in colourless bundles of needles, m. p. 146—147°, and may be reduced by means of sodium amalgam to the known 2-*o*-aminophenylindole (A., 1911, i, 433). The removal of the second portion of hydrogen bromide requires prolonged boiling with alcoholic potassium hydroxide. *Dindole* (II) crystallises from anisole or nitrobenzene in very pale yellow, rhombic crystals, m. p. 320—325° (decomp.).

The closing of the indole ring by means of picric acid solutions can also be effected in the case of the conversion of 2 : 2′-diaminotolane into 2-*o*-aminophenylindole, but not in the case of 2 : 2′-diaminostilbene, probably owing to the fact that the *dipicrate* of this (brown crystals with violet reflex, decomp. 209°) is so sparingly soluble. J. C. W.

The Criss-cross Addition on Conjugate Systems. The Action of Cyanic Acid, Thiocyanic Acid, and *iso*Cyanates on Azines. J. R. Bailey and A. T. McPherson (*J. Amer. Chem. Soc.*, 1917, **39**, 1322—1338).—In a recent paper (this vol., i, 355) it was shown that benzaldazine combines directly with two molecules of cyanic acid. Arguments are now advanced in support of the view that the product has the proposed structure, namely, that of a "5 : 3′-dihydroxy-3 : 5′-diphenyldihydro-1 : 2-triazolotriazole" (annexed formula). This being so, the reaction implies the simultaneous attachment of atomic complexes at the 1 : 3- and 2 : 4-positions of a conjugated system of double linkings, or a "criss-cross" addition. Similar results are obtained in the cases of thiocyanic acid and phenylcarbimide, and the azines of benzaldehyde, *m*-nitrobenzaldehyde, cinnamaldehyde, and furfuraldehyde.



Benzaldazine and phenylcarbimide react at 160—170° to form "5 : 3′-*diketo*-3 : 4 : 4′ : 5′-*tetraphenylhexahydro*-1 : 2-*triazolotriazole*," which crystallises in rhombohedral plates, m. p. 263° (decomposing into phenylcarbimide and benzaldazine, and subsequently nitrogen and stilbene), and yields *benzaldehydephenylcarbamylhydrazone*, NHPh·CO·NH·N:CHPh, as a mass of interlacing needles, m. p. 180°, when heated with potassium hydroxide (1 : 1) at 130°. The hydrazone may be reduced by means of sodium amalgam in boiling alcohol to *α-phenylcarbamyl-β-benzylhydrazine*, prisms, m. p. 138°, oxidised by heating with alcoholic ferric chloride at 130° to 5-*hydroxy*-3 : 4-*diphenyltriazole*, a mass of long, interwoven needles,

m. p. 260°, and hydrolysed by sulphuric acid to benzaldehyde and *phenylsemicarbazide*, $NHPh\cdot CO\cdot NH\cdot NH_2$, m. p. 128°.

Other azines react with phenylcarbimide as follows: *m*-nitrobenzaldazine yields "5 : 3′-*diketo*-4 : 4′-*diphenyl*-3 : 5′-*di*-m-*nitrophenylhexahydro*-1 : 2-*triazolotriazole*," m. p. 260° (decomp.); cinnamaldazine gives "5 : 3′-*diketo*-4 : 4′-*diphenyl*-3 : 5′-*distyrylhexahydro*-1 : 2-*triazolotriazole*," m. p. 243° (decomp.); and furfuraldazine forms "5 : 3′-*diketo*-4 : 4′-*diphenyl*-3 : 5′-*difurylhexahydro*-1 : 2-*triazolotriazole*," m. p. 257° (decomp.).

Cinnamaldazine and furfuraldazine also combine with cyanic acid (potassium cyanate in glacial acetic acid) to form "5 : 3′-*dihydroxy*-3 : 5′-*distyryldihydro*-1 : 2-*triazolotriazole*," m. p. 192° (decomp.), and "5 : 3′-*dihydroxy*-3 : 5′-*difuryldihydro*-1 : 2-*triazolotriazole*," m. p. 191°, respectively. Using potassium thiocyanate and glacial acetic acid, "5 : 3′-*dithiol*-3 : 5′-*difuryldihydro*-1 : 2-*triazolotriazole*," decomp. 154—156°, and "5 : 3′-*dithiol*-3 : 5′-*diphenyldihydro*-1 : 2-*triazolotriazole*" (I), thin, rhombic plates, m. p. 187° (decomp.), may be prepared. The latter forms a sparingly soluble, orange-yellow *compound* with mercuric chloride (1 : 1), and is converted into 5-*thiol*-3-*phenyl*-1 : 2-*benzylidenetriazole* (II), slender prisms, m. p. 166°, when heated with concentrated potassium hydroxide at 150°.

$$N{<}\begin{matrix}CHPh\cdot N\cdot C(SH)\\ C(SH)\cdot N\cdot CHPh\end{matrix}{>}N \qquad N{<}\begin{matrix}CHPh\cdot N\\ C(SH)\cdot N\end{matrix}{>}CHPh.$$

(I.) (II.)

J. C. W.

Methyl- and Ethyl-uric Acids. EINAR BIILMAN and JOHANNE BJERRUM (*Ber.*, 1917, **50**, 837—847. Compare this vol., i, 177; Biltz and Heyn, this vol., i, 292).—The authors have already shown that of the so-called α-, δ-, and ζ-isomerides of 3-methyluric acid, the last two are identical, and by a re-examination of the results of Biltz and Heyn (*loc. cit.*), who have demonstrated that the α-acid contains 3-methyluric acid mixed with some 9-methyluric acid, they are now able to produce evidence that "α-3-methyluric acid" in reality is a molecular compound of 3-methyl- and 9-methyl-uric acids. The evidence is based on concurrent chemical and crystallographic investigation of the "α-acid" and of mixtures of the 3-methyl- and 9-methyl-isomerides in varying proportions. The solubility of the "α-acid" in water exceeds the combined values for the 3-methyl acid and the 9-methyl acid, so that in aqueous solution it must largely retain its bimolecular condition; on the other hand, freezing-point determinations with the "α-acid" and its constituents in alkaline solution indicate that under these conditions the complex molecule of the former acid is almost entirely resolved into a molecule of the 3-methyl acid and one of the 9-methyl acid.

The ethyluric acid known hitherto contains the substituent radicle in the 7- or 9-position; on treating uric acid with ethyl iodide and excess of potassium hydroxide in aqueous solution, a

crystalline 3-*ethyluric acid* is obtained, which can also be formed synthetically by the stages ethyl acetoacetate, methyluracil, potassium nitrouracilcarboxylate, potassium nitrouracil, nitroethyluracil, ethyl*iso*barbituric acid, ethyl*iso*dialuric acid, and ethyluric acid. The presence of the ethyl group in the six-membered ring is confirmed by oxidation of the acid to *diethylalloxantin*, rhombic leaflets, the 3-position being indicated from analogy to the 3-methyluric acid prepared in a similar manner. D. F. T.

Derivatives of Trimethyl-9-ethyluric Acid. HEINRICH BILTZ and MARGARETE BERGIUS (*Annalen*, 1917, **414**, 54—67. Compare this vol., i, 286—300).—A study of the reactions of tetra-alkyluric acids is of especial interest because the triketonic configuration is the only one possible in them. The behaviour of tetramethyluric acid (*loc. cit.*, 299) is now found to be shared by other tetra-alkyl derivatives.

Caffeine is converted into 8-chloro- and then into 8-ethoxycaffeine, and this is heated at 240° in a sealed tube with a little alcohol, when it changes into 1 : 3 : 7-trimethyl-9-ethyluric acid. This acid is accompanied by trimethyluric acid, which is removed by neutralisation with barium hydroxide, the tetra-derivative being extracted from the dried material by means of chloroform. Pure trimethyl-9-ethyluric acid crystallises in aggregates of thin, monoclinic leaflets, m. p. 203—204°, and distils with partial decomposition and liberation of ethylene at about 370°.

When treated with chlorine and methyl alcohol in the cold, the acid yields 4 : 5-*dimethoxy*-1 : 3 : 7-*trimethyl*-9-*ethyl*-4 : 5-*dihydrouric acid*, which crystallises in monosymmetric, limpid tablets, m. p. 97·5°, whilst the less stable 4 : 5-*diethoxy*-derivative, m. p. 142°, is formed in ethyl alcohol. These ethers yield the parent trimethylethyluric acid on heating with hydriodic acid, and 1 : 7-*dimethyl*-3-*ethylcaffolide*, $\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO{-\!\!-}O}\end{array}\!\!>\mathrm{C}<\!\!\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO{-\!\!-}NEt}\end{array}$, m. p. 102°, when boiled with dilute hydrochloric acid. The same product is easily obtained by the action of chlorine on the tetra-alkyluric acid in cold water. The caffolide is hydrolysed by prolonged boiling with water to 5-*hydroxy*-1-*methyl*-3-*ethylhydantoylmethylamide*,

$$\mathrm{CO}<\!\!\begin{array}{l}\mathrm{NMe\cdot C(OH)\cdot CO\cdot NHMe}\\ \mathrm{NEt{-\!\!-}CO}\end{array},$$

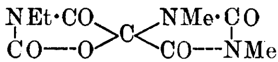
m. p. 140°, and yields 1-*methyl*-3-*ethylhydantoylmethylamide*, m. p. 185°, b. p. 220—230°, on reduction with hydriodic acid.

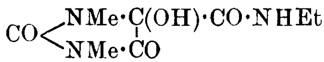
When a suspension of trimethylethyluric acid in glacial acetic acid is treated with chlorine, 1 : 7 : 9-*trimethyl*-3-*ethyl*spiro-5 : 5-*dihydantoin*, $\begin{array}{l}\mathrm{NMe{-}CO}\\ \mathrm{CO\cdot NMe}\end{array}\!\!>\mathrm{C}<\!\!\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO{-\!\!-}NEt}\end{array}$, is obtained, in monoclinic tablets, m. p. 99·5°. J. C. W.

Trimethyl-1-ethyluric Acid and its Derivatives. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 68—78).—Theobromine is converted into 1-ethyl-, 8-chloro-1-ethyl-, and then

8-*methoxy*-1-*ethyl-theobromine*, which crystallises in very slender needles, m. p. 164—165°, and this is transformed by heating at 170° into 3:7:9-*trimethyl*-1-*ethyluric acid*, rhombic tablets, m. p. 176—177°. 4 : 5-*Dimethoxy*-3:7:9-*trimethyl*-1-*ethyl*-4:5-*dihydrouric acid*, m. p. 95°, and the corresponding *diethoxy*-compound, m. p. 105°, are obtained by the action of chlorine in the presence of the appropriate alcohol, and 1:7:9-trimethyl-3-ethyl*spiro*-5:5-dihydantoin (see preceding abstract) by the action of chlorine in glacial acetic acid.

1:3-*Dimethyl*-7-*ethylcaffolide* (I), m. p. 93°, is formed when the tetra-alkyluric acid is treated with chlorine and water, or when the above ethers are boiled with dilute hydrochloric acid, and this is hydrolysed by boiling with water to 5-*hydroxy*-1:3-*dimethylhydantoylethylamide* (II), m. p. 153°:


(I.)


(II.)

The latter compound may be reduced by hydriodic acid to 1:3-*dimethylhydantoylethylamide*, m. p. 196°, b. p. 290° (decomp.), oxidised by chromic acid to dimethylparabanic acid, or hydrolysed by means of barium hydroxide to ethylamine, mesoxalic acid, and dimethylcarbamide. J. C. W.

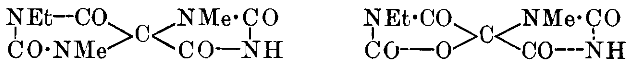
3 : 7-Dimethyl-1 : 9-diethyluric Acid and its Derivatives. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 79—84).—8-Chloro-1-ethyltheobromine is converted into 8-*ethoxy*-1-*ethyltheobromine*, a cotton-wool-like mass of needles, m. p. 153—154°, and this is transformed, by heating at 230° in a sealed tube, into 3:7-*dimethyl*-1:9-*diethyluric acid*, which crystallises in monoclinic tablets, m. p. 158°. 4:5-*Dimethoxy*-3:7-*dimethyl*-1:9-*diethyl*-4:5-*dihydrouric acid*, small rhombohedra, m. p. 78°, and 1:9-*dimethyl*-3:7-*diethyl*spiro-5:5-*dihydantoin*, prisms, m. p. 120°, are obtained in the usual way. 1-Methyl-3:7-diethylcaffolide is likely to be a solid of low melting point, but no crystalline product could be obtained by the action of chlorine and water on the tetra-alkyluric acid. The diethoxy-compound was also not obtained, for under the usual conditions the product was the above *spiro*dihydantoin. The latter is hydrolysed by barium hydroxide to 3:8-*dimethyl*-1:6-*diethylallantoin*, which crystallises in bundles of slender prisms, m. p. 124°. J. C. W.

Derivatives and Degradation of 3 : 7-Dimethyl-1-ethyluric Acid. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 85—98).—This acid was briefly described by E. Fischer (A., 1883, 357), but it has now been examined more thoroughly along the lines of the present research into the alkyluric acids.

The acid, m. p. 345°, may be obtained by hydrolysing 8-ethoxy-1-ethyltheobromine (preceding abstract). It reacts with alcohol and chlorine to form 4:5-diethoxy-3:7-dimethyl-1-ethyl-4:5-dihydrouric acid (Fischer's "diethoxyhydroxyethyltheobromine"). The corre-

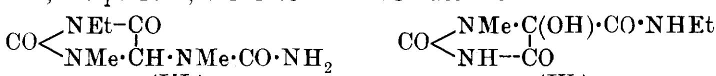
sponding 4:5-*dimethoxy*-3:7-*dimethyl*-1-*ethyl*-4:5-*dihyrouric acid*, rhombohedra, m. p. 178°, can be obtained in the same manner, or more conveniently from 1-ethyltheobromine by the action of chlorine and methyl alcohol. As it is easily reduced to 3:7-dimethyl-1-ethyluric acid by means of stannous chloride, this acid is best prepared by that method.

The authors confirm Fischer's statement that 3:7-dimethyl-1-ethyluric acid yields methylamine, 1:9-dimethyl-3-ethyl*spiro*-5:5-dihydantoin ("hypoethyltheobromine") (I), m. p. 142°, and

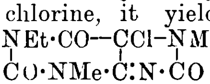


(I.) (II.)

1-methyl-7-ethylcaffolide ("*apo*ethyltheobromine") (II), m. p. 138°, when a solution in concentrated hydrochloric acid is saturated with chlorine at −10° and then evaporated. The *spiro*-compound is best obtained by the action of alcoholic hydrogen chloride on the above ethers, and the caffolide by the action of chlorine and water on 3:7-dimethyl-1-ethyluric acid. The crude, concentrated solution of 1:9-dimethyl-3-ethyl*spiro*-5:5-dihydantoin yields 1:6-*dimethyl*-3-*ethylallantoin* (III), in bundles of long needles, when warmed with barium hydroxide, whilst 1-methyl-7-ethylcaffolide changes into 5-*hydroxy*-1-*methylhydantoylethylamide* (IV), bundles of slender prisms, m. p. 167°, when boiled with water for some time:



(III.) (IV.)

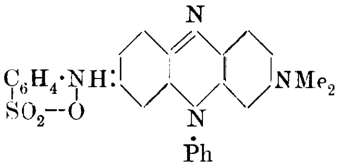
If 3:7-dimethyl-1-ethyluric acid is shaken with glacial acetic acid and chlorine, it yields 5-*chloro*-3:7-*dimethyl*-1-*ethyl*-$\Delta^{4:9}$-iso*uric acid*, , in slender prisms, m. p. about 150° (decomp.). This may be reduced by stannous chloride to the parent acid or converted into the above diethyl ether by means of alcohol.

3:7-Dimethyl-1-ethyluric acid has also been submitted to the usual oxidative degradation, and converted into s-*dimethyldiethylalloxantin*, $C_{14}H_{18}O_8N_4,2H_2O$, hexagonal leaflets or needles, m. p. 174°; *methylethylalloxan*, $C_7H_8O_4N_2,H_2O$, rhombic tablets (*anhydride*, m. p. 124°); and *methylethylvioluric acid*, $C_7H_9O_4N_3,H_2O$, elongated tablets from water, long, hexagonal tablets, m. p. 95—96°, from alcohol (*potassium* salt, reddish-violet with $2H_2O$, violet-blue when anhydrous). J. C. W.

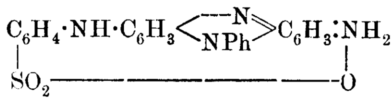
Monosulphonic Acids of Quinone-imide Dyes. F. KEHRMANN and ALEXANDER HERZBAUM (*Ber.*, 1917, **50**, 873—882).—It frequently happens in the dye works laboratory that attempts are made to convert sparingly soluble dyes, especially basic ones, into soluble, acid dyes for wool by sulphonating them, and the usual experience is that one sulphonic acid residue is not sufficient to achieve the desired effect. No explanation of this fact seems to

have been offered, but the obvious suggestion is now made that the monosulphonic acids are internal salts. A number of them are described.

Indazinesulphonic acid (I) is obtained by warming the base with ten times its weight of concentrated sulphuric acid. It crystal-



(I.)

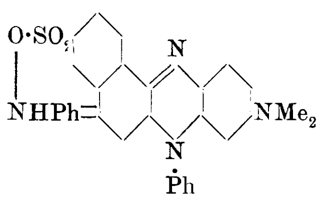


(II.)

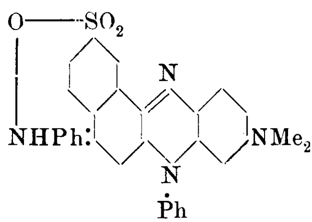
lises in metallic-brown leaflets, gives a green solution in sulphuric acid, which becomes blue and finally violet on dilution, forms a salt in alcoholic potassium hydroxide, but not in aqueous alkali, dyes tanned cotton a good violet shade in warm, dilute acetic acid, and yields sulphanilic acid when heated with hydrochloric acid at 160°.

Phenylphenosafraninesulphonic acid (II) is obtained by oxidising together *p*-phenylenediamine and diphenyl-*m*-phenylenediamine in acetic acid solution with chromic acid, and dissolving the product (ψ-mauveine acetate) in warm sulphuric acid. It crystallises as a reddish-brown, metallic powder, partly with $1H_2O$; it gives a blue solution in alcoholic potassium hydroxide, which becomes violet on diluting, the insoluble dye being reprecipitated.

Naphthindazine-8-sulphonic acid (III) (D.R.-P., 78497) is formed by warming together 1:3-dianilinonaphthalene-7-sulphonic acid, *p*-nitrosodimethylaniline hydrochloride, and sodium acetate in alcohol. It forms brown, metallic crystals, gives a *potassium* salt, which dissolves with reddish-violet colour in water or alcohol, but not in dilute potassium hydroxide, and it scarcely colours tanned cotton. *Naphthindazine-9-sulphonic acid* (IV) is very much like the



(III.)

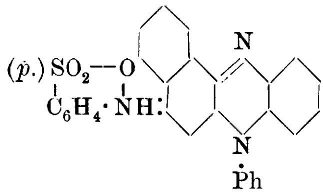


(IV.)

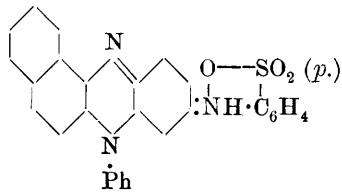
isomeride; it is prepared by condensing *p*-nitrosodimethylaniline with 1:3-dianilinonaphthalene-6-sulphonic acid (from α-naphthylamine-3:6-disulphonic acid and aniline).

Phenylrosindulinesulphonic acid (V) (patented by the Badische Co.) dissolves readily in dilute alkali hydroxides or ammonia, but not in alkali carbonates. It is an inner anhydride, which retains

$1H_2O$ even at 185°. *Phenyl*isoro*sindulinesulphonic acid* (VI) resembles the isomeride, except in being blue.

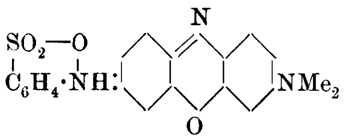


(V.)

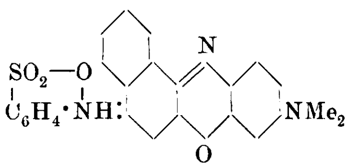


(VI.)

Nitrosodiphenylamine and *m*-dimethylaminophenol give an azoxine dye which dissolves in warm sulphuric acid to form the *sulphonic acid* (VII), which crystallises in bluish-green, brassy needles, with $1H_2O$. It gives violet salts in alkali hydroxide solutions, but not with carbonates, and dyes tanned cotton pale greenish-blue. Phenyl-Nile-blue, from *p*-nitroso-*m*-dimethylamino-

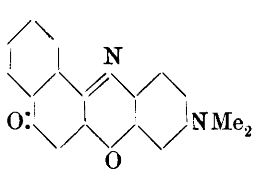


(VII.)



(VIII.)

phenol and 1-anilinonaphthalene (Nietzki and Bossi, A., 1893, i, 44), forms the *sulphonic acid* (VIII) in metallic-green crystals, with $1H_2O$, which give reddish-brown salts with alkali metals, which are insoluble in excess of alkali hydroxide or carbonate. The sulphonation is slow and incomplete, as some of the acid decomposes into *dimethylaminophenonaphthazoxone* (annexed formula). This crystallises from chloroform (the sulphonic acid is insoluble) in large, steely leaflets, m. p. 248—250°. The colours of the solutions and the fluorescence of this compound vary with the refractive index of the solvent, but in the opposite sense to Kundt's rule. The bluish-red solution in alcohol exhibits fiery-red fluorescence; the red, chloroform solution fluoresces yellowish-red; and the orange-red solution in a mixture of ether, benzene, and carbon disulphide has greenish-yellow fluorescence.



J. C. W.

Constitution and Colour. V. The Colour of Azo-compounds and their Salts. II. F. Kehrmann and Stanislas Hempel (*Ber.*, 1917, **50**, 856—872. Compare A., 1916, i, 165).—The absorption spectra, both in the visible and ultra-violet regions, have been determined for azobenzene, *p*-aminoazobenzene, *p*-dimethylaminoazobenzene, *pp'*-diaminoazobenzene, and *pp'*-tetramethyldiaminoazobenzene, in alcohol, acetic acid, alcoholic hydrogen chloride, and concentrated and fuming sulphuric acids. The

results are reproduced by the usual curves, and are discussed in some detail. The authors believe that they are sufficient to show that it is unnecessary to introduce the notion of quinone formation to explain the production of differently coloured salts of aminoazo-compounds. These salts can be regarded as containing different numbers of acid molecules attached to their nitrogen atoms.

J. C. W.

Chromoisomerism of Methyl-orange. WILLIAM M. DEHN and LOIS McBRIDE (*J. Amer. Chem. Soc.*, 1917, **39**, 1348—1377).—A large amount of experimental evidence, mostly of a simple and easily reproducible kind, has been gathered together in proof of the following points. (1) Methyl-orange or helianthin exists in a red, quinonoid form and a yellow, azoid form (compare Hantzsch, A., 1915, i, 322). (2) Aqueous solutions contain the two isomerides in equilibrium. Increased concentration, rise of temperature, or the addition of acids favours the red form; dilution, cooling or the addition of alkali disturbs the equilibrium in the direction of the yellow form. (3) Solutions in absolute phenol contain approximately 100% of the red isomeride; solutions in dry pyridine contain nearly 100% of the azoid form. Compared with these as standards, ordinary aqueous solutions contain 70—99% of the azoid form, even if they are acid, alkaline, or neutral. At great dilutions, helianthin salts, whether of acids or alkalis, are more or less pure yellow; that is, the mass effect of water is to yield the azoid form, regardless of the ionisation of the dye itself. In concentrated solutions, acid salts of helianthin are deep yellowish-red, alkaline salts, light reddish-yellow, that is, both quinonoid and azoid forms are present in each case.

The chief data recorded in this paper are those of the colorimetric comparison of solutions in phenol and pyridine as standards with those in 90% formic acid, *N*-hydrochloric acid, and water, alone or with various acids and bases. The original should be consulted by those engaged in similar studies, but the following facts of general interest may be mentioned. In *N*-hydrochloric acid solutions, on an average 87% of the dye has the azoid configuration, that is, the strong acid is capable of transforming only a small percentage of molecules into the quinonoid type. Pure helianthin averages about 97·7% of azoid molecules in water. In the presence of 1, 10, and 100 molecular proportions of sodium hydroxide, the azoid concentrations are 98·28, 98·59, and 98·67% respectively; that is, even much strong alkali does not give pure yellow solutions. Some of each chromoisomeride is present in any aqueous solution, and, therefore, in view of the disturbing influence of water on the equilibria, the concentration of the dye should be maintained constant in all accurate titrations.

J. C. W.

Colorimetric Determination of the Solubilities of Helianthin and its Salts. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1377—1381).—The solubility of helianthin in some acids, phenols, bases, alcohols, esters, aldehydes, ketones, ethers,

hydrocarbons, and other organic media, water, and saturated solutions of salt and sugars, has been determined by diluting 1 c.c. portions of the solutions to 250 c.c. with *N*-hydrochloric acid and matching the colour against standard solutions of pure helianthin in *N*-HCl. Helianthin is insoluble in hydrocarbons and their halogen, nitro-, and alkyloxy-derivatives; it forms soluble, red salts with certain acids and yellow salts with certain bases, but it also gives alternately red or yellow solutions in "indifferent" solvents, provided these contain chemically active groups (aldehyde or ketone) or labile hydrogen atoms. Even "indifferent" solvents have chemical action on helianthin, just as water has in changing the quinonoid into the azoid form. Possibly they combine with the amino- or sulphonic groups in helianthin, ano so lead to one or other of the tautomeric forms. J. C. W.

Comparison of Phenylhydrazine Oxalate with Mesoxalic Acid Phenylhydrazone. W. L. EVANS, W. L. MONG, and F. L. SINKS (*J. Amer. Chem. Soc.*, 1917, **39**, 1724—1727).—New conditions are described for the preparation and analysis of phenylhydrazine oxalate, with which the compound described by Causse (A., 1894, i, 569) as mesoxalic acid phenylhydrazone is shown to be identical.

Basic bismuth mesoxalate, $Bi(OH)(C_3O_5),2H_2O$, prepared by a method similar to that used by Vanino and Zumbusch (A., 1909, ii, 56) for obtaining normal bismuth oxalate, forms a white precipitate. When treated with hydrogen sulphide, and the product thus obtained with phenylhydrazine, it yields mesoxalic phenylhydrazone, whereas Vanino and Zumbusch's normal oxalate and Causse's bismuth mesoxalate (*loc. cit.*) yield phenylhydrazine oxalate under similar conditions. T. H. P.

Phenyl-2 : 6-dinitrobenzylhydrazine. S. REICH (*Bull. Soc. chim.*, 1917, [iv], **21**, 114—117).—[With G. GAIGAILIAN and P. CHASKELIS.]—2 : 6-Dinitrobenzyl bromide when boiled in alcoholic solution with phenylhydrazine, yields as-*phenyl*-2 : 6-*dinitrobenzylhydrazine*, $NH_2\cdot NPh\cdot CH_2\cdot C_6H_3(NO_2)_2$, red crystals, m. p. 106—107°, and s-*phenyl*-2 : 6-*dinitrobenzylhydrazine*,

$$NHPh\cdot NH\cdot CH_2\cdot C_6H_3(NO_2)_2,$$

a viscid, red oil. The latter compound does not undergo ring-formation in the presence of alcoholic potassium hydroxide, but on exposure to air is oxidised to 2 : 6-dinitrobenzaldehydephenylhydrazone. The solid unsymmetrical hydrazine gives with nitrous acid *phenyl*-2 : 6-*dinitrobenzylnitrosoamine*, $NO\cdot NPh\cdot CH_2\cdot C_6H_3(NO_2)_2$, m. p. 116°, and with pyruvic acid it yields *pyruvic acid phenyl*-2 : 6-*dinitrobenzylhydrazone*, pale pink needles, m. p. 145—146°. W. G.

Picryl Azide. ERNST SCHRADER (*Ber.*, 1917, **50**, 777—778).—Picryl azide can be conveniently prepared by the interaction of picryl chloride and sodium azide in aqueous-alcoholic solution. The pure substance forms yellow prisms, m. p 93° (compare Purgotti,

A., 1895, i, 27), and when heated with benzene or xylene loses a molecular proportion of nitrogen with the formation of 2:4-dinitro-1:6-dinitrosobenzene. It is only feebly explosive. D. F. T.

Tritico-Nucleic Acid. B. E. READ and W. E. TOTTINGHAM (*J. Biol. Chem.*, 1917, **31**, 295—301).—Tritico-nucleic acid prepared from the wheat embryo yields on hydrolysis the same products as yeast-nucleic acid (compare Jones and Read, this vol., i, 232, 233). Since in all its other properties tritico-nucleic acid closely resembles yeast-nucleic acid, it is probable that these two substances are really identical. H. W. B.

Uracil-Cytosine-Dinucleotide. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **31**, 39—45. Compare this vol., i, 233).—When yeast-nucleic acid is heated with dilute sulphuric acid, its central nucleotide linking is not disturbed, but the two terminal nucleotide linkings are broken and *uracil-cytosine-dinucleotide* is formed. The dinucleotide, $C_{18}H_{25}O_{16}N_5P_2$, is obtained as a white, granular powder, $[\alpha]_D$ $+15{\cdot}0^\circ$. On boiling with dilute sulphuric acid, it is slowly decomposed into its constituent pyrimidines, phosphoric acid, and carbohydrate. The decomposition is hastened by employing 25% sulphuric acid and heating in an autoclave at 140°; indeed, this constitutes a good and quick method for the preparation of cytosine and uracil. On heating in an autoclave with 2% ammonium hydroxide at 140°, the dinucleotide yields uridine and cytidine.

On treatment of the dinucleotide with brucine in alcoholic solution, a crystalline *brucine* salt is formed,

$$C_{18}H_{25}O_{16}N_5P_2,4(C_{23}H_{26}O_4N_2),14H_2O.$$

It is obtained in needles which sinter at 170° and melt at 175°. The same conduct is exhibited by the brucine salt of adenine-uracil-dinucleotide, and is apparently a brucine phenomenon, as it occurs at the melting point of brucine (175°). H. W. B.

Guanine-Mononucleotide (Guanylic Acid) and its Preparation from Yeast-Nucleic Acid. B. E. READ (*J. Biol. Chem.*, 1917, **31**, 47—53).—When yeast-nucleic acid is heated with 2·5% ammonium hydroxide in an autoclave at 115°, the ammonium salt of guanine-mononucleotide is formed, and is readily separated by precipitation with alcohol. The lead salt is then formed by dissolving in water, acidifying with acetic acid, and treating with lead acetate. The free mononucleotide is afterwards liberated by hydrogen sulphide, and on concentration of the filtrate is obtained as a white, amorphous powder, $[\alpha]_D$ $-2{\cdot}4^\circ$. It forms a *brucine* salt, $C_{10}H_{14}O_8N_5P,2(C_{23}H_{26}O_4N_2),7H_2O$, m. p. 203°, which on keeping in a vacuum desiccator over sulphuric acid rapidly loses water, which is slowly taken up again on exposure to the air. The substance readily parts with its phosphoric acid on warming with dilute sulphuric acid, like other purine-nucleotides.

Specimens of guanylic acid prepared from the pancreas of the

pig or the ox have properties which are identical with those of guanine-mononucleotide from yeast-nucleic acid. H. W. B.

Structure of the Purine Mononucleotides. WALTER JONES and B. E. READ (*J. Biol. Chem.*, 1917, **31**, 337—342. Compare this vol., i, 232).—On hydrolysis with dilute sulphuric acid, guanine mononucleotide liberates guanine with much greater rapidity than it liberates phosphoric acid. The mononucleotide must therefore have the structure $C_5H_4ON_5 \cdot C_5H_8O_3 \cdot O \cdot PO(OH)_2$, and not the alternative $C_5H_9O_4 \cdot C_5H_3ON_5 \cdot PO(OH)_2$. Adenine–uracil–dinucleotide similarly liberates its adenine far more rapidly than it liberates its phosphoric acid. As the two phosphoric acid groups of the dinucleotide are not directly joined to one another (compare Jones and Read, this vol., i, 233), it follows that adenine mononucleotide must also have a similar structure to that of the guanine mononucleotide. H. W. B.

The Absorption of Light by Oxyhæmoglobin. PAUL HÁRI (*Biochem. Zeitsch.*, 1917, **82**, 229—281).—A detailed investigation of the absorption of light of various wave-lengths by solutions of oxyhæmoglobin, and a comparison of the results obtained by previous investigators, chiefly Butterfield and Hüfner. S. B. S.

Enzyme Action. XV. Factors Influencing the Proteolytic Activity of Papain. EDWARD M. FRANKEL (*J. Biol. Chem.*, 1917, **31**, 201—215).—Commercial papain can be purified by precipitating the aqueous suspension of the powder with acetone or alcohol. The purified enzyme exerts its optimum action in a medium of which the hydrogen-ion concentration is 10^{-5}. Its activity is inhibited by both acids and alkalis, the latter being less destructive.

Papain resembles other enzymes in forming an intermediate compound with its substrate, which is subsequently broken up into the cleavage products with the liberation of unchanged enzyme. In the presence of hydrocyanic acid, the proteolytic action is intensified (compare Mendel and Blood, A., 1910, i, 796), and apparently the intermediate compound formed contains hydrocyanic acid, as well as papain and substrate. In the second stage of the action, the cleavage products are liberated, whilst both the hydrocyanic acid and the enzyme may be recovered almost quantitatively from the digestion mixtures. H. W. B.

Influence of Certain Electrolytes on the Course of the Hydrolysis of Starch by Malt Amylase. H. C. SHERMAN and JENNIE A. WALKER (*J. Amer. Chem. Soc.*, 1917, **39**, 1476—1493).—Having already determined the concentrations of hydrochloric acid, phosphoric acid, or potassium dihydrogen phosphate, which favour optimum activity of purified malt amylase (A., 1915, i, 183), the authors have been able to study the rate of formation of reducing sugar from soluble starch under various conditions.

The saccharogenic action of the enzyme is found to be increased by the addition of the optimum amounts of electrolytes, not only in the early stages, but throughout. The greater the concentration of enzyme, the less is the benefit derived from the electrolytes; with 0·0012% of the enzyme acting on a 1% solution of starch, the hydrolysis is as rapid and complete without electrolytes as with.

When more than the optimum amount of acid is added, the hydrolysis proceeds at a slower rate than the best throughout. This inhibitory effect is most marked with hydrochloric acid, less with phosphoric, and least with potassium dihydrogen phosphate. Probably, owing to secondary ionisation, the optimum H-ion concentration is maintained in the latter cases ("buffer effect"). With less than the optimum amount of electrolyte, the original speed of hydrolysis is sustained better than with too much electrolyte.

Up to the point at which half the theoretical amount of sugar has been formed, provided that favourable amounts of electrolyte are present, the speed of hydrolysis is proportional to the concentration of starch and of enzyme. There seems to be no region in which the yield of sugar is directly proportional to time, nor is there any cessation of hydrolysis or establishment of an equilibrium when 80% of the possible yield is obtained, as some have supposed. Even the comparatively resistant dextrins which remain towards the end are attacked, but at a very slow rate. J. C. W.

A Noteworthy Effect of Bromides on the Action of Malt Amylase. ARTHUR W. THOMAS (*J. Amer. Chem. Soc.*, 1917, **39**, 1501—1503).—Whereas the chlorides, nitrates, sulphates, and phosphates of sodium and potassium activate purified malt amylase in proportion to their concentrations (A., 1915, i, 183), the bromides exert an inhibitory effect when present in small amounts, but an activating influence in greater concentrations. J. C. W.

Enzyme Action. XIV. Further Experiments on Lipolytic Actions. K. GEORGE FALK (*J. Biol. Chem.*, 1917, **31**, 97—123. Compare Falk and Sugiura, A., 1915, i, 92).—From a study of the numerous ways in which inactivation of lipase and esterase may be accomplished, the author is led to suggest that the activity of these enzymes is associated with the presence of the grouping —C(OH)⁚N—, and that inactivation occurs when this grouping is converted into the tautomeric —CO·NH— structure. In support of this hypothesis, it is found that dipeptides containing the above specified grouping exert a distinct hydrolytic action on ethyl butyrate and glyceryl triacetate, and that the addition of alkali, which presumably favours the production of the enolic tautomeride, is accompanied by a distinct increase in the hydrolytic power of the dipeptide. The author demonstrates by means of control experiments that it is not the increased alkalinity of the solutions which is chiefly responsible for the increased hydrolysis. It is also noted that equimolecular quantities of different

dipeptides produce the same amount of hydrolysis of glyceryl triacetate in the same time.

The simple amino-acids, which do not contain the —C(OH):N— grouping, exert a relatively small hydrolytic action on glyceryl triacetate and ethyl butyrate. Comparison of the hydrolytic effects produced by an amino-acid and the corresponding dipeptide renders it possible to assign a definite hydrolytic value to the —C(OH):N— grouping, which is the same, within limits, no matter from which pair of related substances the value is calculated.

Substances containing the —C(OR):N— grouping, such as ethyl iminobenzoate, $C_6H_5\cdot C(NH)\cdot OEt$, resemble the naturally occurring lipases in that a maximum hydrolytic action is obtained at a definite hydrogen-ion concentration, and that the activity disappears when the substance is changed by the action of acids or alkalis, or by heating or even prolonged keeping in solution.

Partial hydrolysis of proteins probably produces substances possessing the —C(OH):N— grouping, and the author notes that proteins treated with alkalis exert marked hydrolytic action on esters, even after the free alkali has been removed by neutralisation or dialysis. H. W. B.

Metallic Derivatives of Diaminodihydroxyarsenobenzene. J. DANYSZ (Eng. Pat., 104496; from *J. Soc. Chem. Ind.*, 1917, **36**, 906).—The compounds obtained from 3:3′-diamino-4:4′-dihydroxyarsenobenzene and mercury salts are difficult to use therapeutically, since they are only slightly soluble in dilute acids and decompose when sodium hydroxide is added. If, however, they are treated with antimony compounds, antimonyl derivatives are obtained which are more soluble, stable in alkaline solution, more active, and less toxic. T. S. P.

Metallic Derivatives of Diaminodihydroxyarsenobenzene. J. DANYSZ (Brit. Pat., 104497; from *J. Soc. Chem. Ind.*, 1917, **36**, 907).—One mol. of 3:3′-diamino-4:4′-dihydroxyarsenobenzene hydrochloride is treated in aqueous solution with 1 mol. of a freshly prepared silver haloid, and 1 mol. of antimony trichloride is dissolved in the solution by heating; to the resulting solution is added a concentrated solution of citric acid; dilute sulphuric acid is then added to precipitate the base. The silver salt may be replaced by the salts of gold, platinum, or copper. The stable products obtained are much more antiseptic and relatively less toxic than the parent substance. T. S. P.

Arsenic Compounds of the Anthraquinone Group. L. BENDA (*J. pr. Chem.*, 1917, [ii], **95**, 74—106).—α-Aminoanthraquinone, by diazotisation in concentrated sulphuric acid, was converted into the corresponding diazo-compound, which on treatment with a solution of sodium arsenite in the presence of sodium carbonate, gave rise to colourless *anthraquinone-1-arsinic acid*,

$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}AsO_3H_2$, colourless needles. This substance is reduced by sodium hyposulphite in alkaline aqueous solution at 50° with formation of 1 : 1'-*arsenoanthranol*,

$$As_2\left[C_6H_3{<}^{C(OH)}_{C(OH)}{>}C_6H_4\right]_2,$$

a deep brownish-red substance, which gives yellow solutions in alcohol and ether, but a blood-red solution in aqueous sodium hydroxide; when exposed to the atmosphere this alkaline solution undergoes rapid oxidation with re-formation of the arsinic acid, but in the presence of sodium carbonate, atmospheric oxidation of the arsenoanthranol proceeds only to yellow *anthraquinone-1-arsenoxide*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}AsO$, for the further oxidation of which to anthraquinonearsinic acid hydrogen peroxide is necessary. Anthraquinone-1-arsinic acid, when heated strongly, undergoes decomposition with formation of erythrohydroxyanthraquinone, $C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}OH$, arsenious oxide and water; on reduction with sodium amalgam in alkaline solution, it undergoes fission into anthraquinone and arsenious acid, the ease of this change probably accounting for the high toxicity of the arsinic acids of the anthraquinone group.

Anthraquinone-2-arsinic acid, prepared by a similar process to that adopted for its 1-isomeride, forms yellow needles, which remain unfused at 270°; like the 1-compound, it gives precipitates with calcium chloride and with magnesia mixture in ammoniacal solution at the ordinary temperature. Anthraquinone-2-arsinic acid is relatively resistant to the action of sodium amalgam and aqueous alkali, this behaviour being in accord with the fact that it is much less poisonous than the isomeric 1-arsinic acid.

4-Aminoanthraquinone-1-arsinic acid, $C_{14}H_{10}O_5NAs$ (*sodium* salt, red needles with $4H_2O$), was obtained as a red, crystalline powder, m. p. indistinct at 278° (decomp.), by the interaction of an alkaline solution of sodium arsenite with the product formed on diazotising 1 : 4-diaminoanthraquinone in diluted sulphuric acid. The product of diazotisation in concentrated sulphuric acid, using an excess of nitrosylsulphuric acid, reacted with sodium arsenite, forming *4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_9O_6As$, yellow needles, decomp. above 200° (*sodium* salt, brownish-yellow needles); this yielded a brownish-red precipitate with magnesia mixture at the ordinary temperature, and in solution in sulphuric acid could be nitrated to *3-nitro-4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_8O_8NAs$, yellow needles, decomp. near 230°, the constitution of which was demonstrated by reduction with ferrous hydroxide to aminohydroxyanthraquinone, m. p. near 250°, and conversion of this into alizarin by heating with hydrochloric acid at 250°. Reduction of 3-nitro-4-hydroxyanthraquinone-1-arsinic acid with a restricted quantity of ferrous hydroxide yielded *3-amino-4-hydroxyanthraquinone-1-arsinic acid*, $C_{14}H_{10}O_6NAs$, violet, silky needles, m. p. near 265°, the arsenic-containing radicle escaping elimination

under these conditions. The product formed a *hydrochloride* and gave a crystalline *diazo*-compound (needles), which coupled with *R*-salt and with resorcinol, producing violet- and blue-coloured solutions respectively; it was also reducible by sodium hyposulphite to an orange-coloured vat, which imparted a violet stain to filter-paper.

1 : 5-Diaminoanthrarufin was converted by way of its chocolate-brown, crystalline tetrazo-compound into 4 : 8-*dihydroxyanthraquinone*-1 : 5-*diarsinic acid* (*anthrarufindiarsinic acid*), $C_{14}H_{10}O_{10}As_2$, a yellow, microcrystalline powder, decomp. above 270°, the violet-coloured *disodium* salt of which gave in aqueous sodium hydroxide an orange-coloured solution presumably of the *tetrasodium* salt. On nitration in sulphuric acid at 80° this arsinic acid yielded 3 : 7-*dinitro*-4 : 8-*dihydroxyanthraquinone*-1 : 5-*diarsinic acid*,

$$C_{14}H_8O_{14}N_2As_2,$$

a greenish-yellow, microcrystalline powder, the violet *disodium* salt of which, on successive treatment in solution with aqueous sodium hydroxide and alcohol, formed a bluish-red precipitate, presumably of the tetrasodium derivative. By treatment in alkaline aqueous solution with sodium amalgam, the dinitro-diarsinic acid was reducible to 3 : 7-*diamino*-4 : 8-*dihydroxyanthraquinone*-1 : 5-*diarsinic acid*, $C_{14}H_{12}O_{10}N_2As_2$, a dark violet powder with metallic reflex; *disodium* salt, crystalline with a coppery lustre. D. F. T.

Physiological Chemistry.

The Hydrogen Number and Oxygen-combining Power of the Blood. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1917, **82**, 282—288).—The constant k of Hill's formula, $y/100 = kx^{2\cdot5}/1 + kx^{2\cdot5}$, where $y = \%$ of complete saturation and $x =$ oxygen tension, was determined with varying p_H for different bloods, the p_H being determined by the method recently described by the author (the estimation of free and bound carbon dioxide in the blood). If $-\log k$ is plotted on the ordinates and p_H on abscissa, a straight line is obtained, which in normal cases is the same as that obtained by Barcroft and Peters with the blood of Barcroft, that is, in normal cases, a given reaction of the blood corresponds with a definite value of the constant k. This does not hold, however, for certain pathological cases, and for this reason Barcroft's method of determining the reaction by estimation of the oxygen-combining capacity will not always give the correct results. S. B. S.

Uric Acid Content of the Blood of New-born Children. F. B. KINGSBURY and J. P. SEDGWICK (*J. Biol. Chem.*, 1917, **31**, 261—268).—There is a striking parallelism between the high uric

acid content of the blood and of the urine of new-born children. This supports the view that the human fœtal tissues are devoid of uricolytic power (compare Wells and Corper, A., 1909, ii, 749).

H. W. B.

The Assumed Destruction of Trypsin by Pepsin and Acid. III. Observations on Men. J. H. Long and Mary Hull (*J. Amer. Chem. Soc.*, 1917, **39**, 1493—1500. Compare this vol., i, 361).—Experiments on men confirm the results obtained with dogs, that trypsin may resist the action of pepsin and acid for a considerable period in the stomach, even when the conditions are by no means abnormal. The plan of the work was as follows. A test meal was given, and after a time the stomach-content was drawn off by a tube and examined for acid, pepsin, bile, and possible tryptic action. If the conditions appeared to be normal, trypsin was fed with the meal and the stomach-content examined again. Tryptic activity was measured by the ability of the liquid to digest fibrin in a slightly alkaline medium, the factor recorded being the result of a formaldehyde amino-acid titration. If bile were found in the stomach, it would naturally suggest that trypsin had also been carried back by the regurgitation of duodenal fluid, but even when no bile was present the tryptic activity, due to the ingested ferment, was quite well marked, provided the acidity was not too great.

J. C. W.

Influence of Bile on the Production of Phenol. Harry Dubin (*J. Biol. Chem.*, 1917, **31**, 255—259. Compare A., 1916, i, 695).—By means of surgical procedures, it is possible to prevent the flow of bile into the small intestine. In the case of two dogs, an anastomosis was produced between the bile duct and the ureter, so that the bile passed directly into the urine. In another case an external bile fistula was produced, whereby it was possible to collect the bile so that the urine was free from it. It is found that, in these circumstances, large amounts of phenol are produced, unaccompanied by any increase in the conjugated acids. The increased production of phenol is due probably to the increased decomposition of the intestinal contents brought about by the diminished digestive activity caused by the absence of bile from the intestine. There is also a diminished inhibition of bacterial fermentative secretions. The unchanged conjugation indicates impaired liver function, or slow production of the phenol, or a combination of both.

H. W. B.

Hydrogen-ion Concentration of the Contents of the Ileum. J. F. McClendon, A. Shedlov, and W. Thomson (*J. Biol. Chem.*, 1917, **31**, 269—270. Compare McClendon, A., 1915, i, 915).—In pups, the contents of the ileum are slightly acid throughout the nursing period and, later, on a diet of solid food. The acidity ($p_H = 6{\cdot}3$) is less than the acidity of the contents of the duodenum in children during the first few days after birth ($p_H = 3{\cdot}1$).

H. W. B.

Metabolism of Sulphur. II. Influence of Small Amounts of Cystine on the Balance of Nitrogen in Dogs maintained on a Low Protein Diet. HOWARD B. LEWIS (*J. Biol. Chem.*, 1917, **31**, 363—377).—The addition of small amounts of cystine to the food of dogs on a low protein diet diminishes the loss of nitrogen from the body, and thus favourably influences the nitrogen balance. This is interpreted to be the result of a specific demand for the sulphur-containing cystine for metabolic purposes, since tyrosine and glycine added to the diet under similar conditions of experimentation do not diminish the loss of nitrogen or influence the state of nitrogenous equilibrium. H. W. B.

Calcium and Magnesium Metabolism. I. Effects of Alkali and Acid. MAURICE H. GIVENS and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1917, **31**, 421—433).—The addition of acids or alkalis to the food of dogs does not produce any significant change in the balance of nitrogen, calcium, magnesium, or phosphorus in the dog. The administration of hydrochloric acid increases the amount of calcium excreted in the urine at the expense of that excreted in the fæces; the relation of calcium to magnesium in the urine is thereby changed. The calcium in milk is retained more readily by the body than the calcium in calcium lactate. In diabetes, the administration of large doses of alkali hydrogen carbonate does not decrease the output of calcium in the urine.
H. W. B.

Calcium and Magnesium Metabolism. II. Effect of Diets Poor in Calcium. III. Effect of Fat and Fatty Acid Derivatives. MAURICE H. GIVENS (*J. Biol. Chem.*, 1917, **31**, 435—439, 441—444).—A definite relation between the output of calcium and nitrogen in dogs does not exist, and even when the diet is poor in calcium salts, storage of calcium does not occur, the calcium balance being negative. When the fat in the diet escapes absorption, the output of calcium is also increased, due to excretion of insoluble calcium soaps in the fæces. Large quantities of fatty acids in the diet likewise occasion a loss of calcium from the body. H. W. B.

Comparative Metabolism of certain Aromatic Acids. CARL P. SHERWIN (*J. Biol. Chem.*, 1917, **31**, 307—310).—Phenylacetic acid administered to a monkey (*Macacus rhesus*) reappears in the urine in combination with glycine as phenylaceturic acid. The same change occurs after feeding dogs, rabbits, horses, and other lower animals with the substance. In the case of man, ingested phenylacetic acid is excreted partly as phenylacetylglutamine and partly as phenylacetylglutamine-carbamide (Thierfelder and Sherwin, A., 1915, i, 481). The monkey, therefore, is to be classed with the other lower animals rather than with man when judged from the point of view of the metabolic treatment of ingested phenylacetic acid. H. W. B.

Rôle of Vitamines in the Diet. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1917, **31**, 149—163).—The addition of 1·5%

of dried yeast to a diet of purified caseinogen, starch, lard, butter-fat, and artificial protein-free milk greatly increases its power to produce growth in rats. When, however, caseinogen is replaced by edestin, lactalbumin, or a vegetable protein, young rats fail to grow, although adult rats can be maintained in health over long periods. These results are surprising, especially in the case of lactalbumin, which has been shown to be capable of producing normal growth when present in comparatively small proportion in the diet (A., 1916, i, 690). Rats growing on the diet containing yeast and caseinogen cease to thrive immediately the yeast is withdrawn.

Experiments are described the results of which show that the rapidity of growth is related to the amount of yeast added to the food. In general, a proportion of 1·5% to 2% of yeast in the food is sufficient to produce normal growth. The yeast appears to have a direct action on the processes of growth and does not merely stimulate appetite. It is the improvement in the general condition of the animal caused by the addition of yeast to the diet which leads to the increase in the appetite.

The concentrated aqueous extract of yeast possesses the same stimulating capacity on the growth of rats as the yeast itself. These experiments confirm the presence in yeast of the so-called water-soluble vitamine (McCollum and Kennedy, A., 1916, i, 451).

H. W. B.

Vitamine Hypothesis and Deficiency Diseases. Experimental Scurvy. E. V. McCollum and W. Pitz (*J. Biol. Chem.*, 1917, **31**, 229—253).—The authors describe experiments in which guinea-pigs are fed on a diet which, although adequate to maintain rats in good health for indefinite periods, leads to the development of scurvy in these animals. These results are attributed, not to the absence of a specific protective substance or anti-scorbutic vitamine, but to a retention of fæces in the cæcum owing to the unfavourable physical character of the diet, and to a consequent debility of the digestive tract through stretching and contact with irritating and toxic putrefaction products of bacterial origin. The addition to the diet of substances which depress the growth of micro-organisms in the digestive tract, such as sodium benzoate or citric acid, or which facilitate the elimination of the fæces, such as liquid petroleum, phenolphthalein, or orange juice, appears to prevent the development of scurvy; and, further, animals in which the scorbutic condition has been allowed to become pronounced are cured by the addition of these substances to the original diet.

The results are graphically illustrated by charts. H. W. B.

Nutrition Investigations on Cotton-seed Meal. III. Cotton-seed Flour. The Nature of its Growth-promoting Substances, and a Study in Protein Minimum. Anna E. Richardson and Helen S. Green (*J. Biol. Chem.*, 1917, **31**, 379—388. Compare this vol., i, 524).—Rats are fed on a diet of caseinogen, lard, starch, and mineral matter, together with varying

amounts of the aqueous and ethereal extracts of cotton-seed flour. Normal growth is attained when the amount of water-soluble accessory substance added to the food is equivalent to that which would have been present if 50% of the diet had consisted of cotton-seed flour. Similarly, the requisite amount of ether-soluble accessory substance is that which can be extracted from cotton-seed flour equivalent to 138% of the diet.

Experiments are also described in which cotton-seed flour constituted the sole source of protein in the diet, adequate supplies of other necessary ingredients being furnished by suitable materials. Under these conditions, normal growth of rats and their offspring is achieved when the diet contains not less than 18% of cotton-seed flour. H. W. B.

Nutritive Value of the Diamino-acids occurring in Proteins for the Maintenance of Adult Mice. E. M. K. Geiling (*J. Biol. Chem.*, 1917, **31**, 173—199. Compare Ackroyd and Hopkins, this vol., i, 237; and Abderhalden, A., 1916, i, 580).—The removal of the diamino-acids from hydrolysed caseinogen by means of phosphotungstic acid renders it no longer adequate for the maintenance of adult mice when it constitutes the sole source of nitrogen in their diet. If, now, cystine and either arginine or histidine are added, the efficiency of the diet is restored. Apparently arginine and histidine may completely replace each other in a diet without affecting its efficiency, whilst the presence of lysine is unnecessary for the maintenance of mice.

The disappearance of the nutritive efficiency of caseinogen on heating for an hour in an autoclave at 7 kilos. pressure is confirmed (McCollum and Davis, A., 1916, i, 183). H. W. B.

How are the Plant Proteins of the Diet Utilised in the Animal Body? II. H. Boruttau (*Biochem. Zeitsch.*, 1917, **82**, 96—102. Compare A., 1915, i, 616).—To dogs, after an interval of nitrogen-free diet, were administered diets containing known amounts of nitrogen of vegetable origin; a period of nitrogen-free feeding followed. The nitrogen excreted in urine and fæces during these periods was estimated, and from the results the biological value was calculated by the two formulæ of Thomas. The results seem to indicate that the physiological evaluation of the proteins is somewhat complex, as no very definite conclusions are to be drawn from the limited number of experiments described. S. B. S.

Permeability of Cells. VII. Resorption of Proteins and their Degradation Products from the Peritoneal Cavity of the Rabbit. Marcus Kjöllerfeldt (*Biochem. Zeitsch.*, 1917, **82**, 188—225. Compare A., 1916, i, 450).—It was difficult to determine the resorption of casein, owing to the formation of exudates. Of peptone introduced into the peritoneal cavity, 15% was absorbed in thirty minutes and 24% in sixty minutes; 40% of hydrolysed casein was absorbed in sixty minutes; 50—65% of

amino-acids were absorbed in sixty minutes. There was an appreciable difference in the rate of absorption of the different amino-acids, but an insufficient number of experiments have been carried out to determine accurately their relative absorbability.

S. B. S.

Proteoclastic Tissue Enzymes of the Spleen. MAX MORSE (*J. Biol. Chem.*, 1917, **31**, 303—306).—The proteins of the spleen are hydrolysed during autolysis by a proteoclastic enzyme which operates only in a neutral, or preferably slightly acid, medium, and corresponds with the β-protease described by Hedin (A., 1904, ii, 58). The other enzyme in the spleen, α-protease, exerts its action in an alkaline medium and hydrolyses peptone or fibrin, but is without action on the native proteins of the spleen. The latter enzyme is therefore not a true autolytic enzyme, and probably is derived from the leucocytes in the spleen instead of from true splenic tissue.

H. W. B.

Transformation of Arginine into Creatine in the Animal Organism. B. C. P. JANSEN (*Arch. Néerland. Physiol.*, **1**, 618—624. Compare Thompson, this vol., i, 369).—An increase in the tonus of a muscle is known to be attended by the production of creatine (Pekelharing and van Hoogenhuyze, A., 1910, ii, 324). It is now shown that increased tonus is accompanied by a disappearance of arginine which corresponds in amount with the creatine produced in the muscle. The author draws the conclusion that creatine is formed directly from arginine.

The amount of arginine in muscle is estimated after hydrolysis by treating equal parts of the neutralised hydrolysate with urease, and a mixture of urease and arginase respectively. After incubation, the amount of arginine is calculated from the difference in the amounts of ammonia obtained by distillation from the two portions.

H. W. B.

A New Olfactometer. C. VAN DAM (*Arch. Néerland. Physiol.*, 1917, **1**, 660—665).—The odoriferous material is mixed in any desired proportion with 10 grams of melted paraffin (m. p. 60°) and cast into cylinders 3·5 cm. long and 0·6 cm. in diameter. These are fixed into small copper tubes 1½ cm. in length, which can be screwed on to a copper rod, 10 cm. in length.

The olfactometer is made of glass, and consists of an air tube, 1·5 cm. in diameter and 16 cm. long, into one end of which two tubes are fused, each 8 cm. long and 0·6 cm. diameter, at right angles to each other. One of these, the carrying tube, into which the odoriferous cylinder slides, has the same axis as the air-tube and penetrates it to a depth of 6 cm. The other, to the outer end of which the nose is applied, is perpendicular to the air and carrying tubes. The odoriferous cylinder, with its attachments, is placed in the carrying tube and gently pushed in until a smell is just perceived by the nose at the end of the perpendicular tube. The cylinder is then pushed just a little further until the odour is

distinctly recognised. The length of the wax cylinder which emerges from the internal aperture of the carrying tube is taken as a measure of the odoriferous power of the material experimented with.

Certain advantages relating to simplicity of apparatus and accuracy of results are claimed for this method as compared with that of Zwaardemaker. H. W. B.

Adsorption of Odoriferous Substances. C. VAN DAM (*Arch. Néerland. Physiol.*, 1917, **1**, 666—677).—The author investigates the relative power of different materials, such as gold, silver, platinum, iron, wood, ebonite, glass, quartz, bone, etc., to adsorb the odour of certain volatile liquids, ionone, eugenol, acetophenone, nitrobenzene, etc.

A drop of the odoriferous liquid is placed by means of a thin rod on the bottom of a cylindrical flask, which is then stoppered. When the odour has become uniformly distributed, a cylinder of the material the adsorptive capacity of which is to be measured is introduced into the flask and allowed to remain in contact with the vapour for one minute. It is then withdrawn, and the amount of odoriferous substance adsorbed is measured by means of the olfactometer previously described (compare preceding abstract). The procedure is then repeated with a cylinder of another material.

The results are variable, and, although there are indications of the dependence of the degree of adsorption of the odour of various substances on their chemical constitution, the author nevertheless draws the conclusion that definite quantitative relations cannot yet be established. H. W. B.

Adsorption of Odoriferous and other Substances by Lipoids. J. H. KREMER (*Arch. Néerland. Physiol.*, 1917, **1**, 715—725).—By means of a spectroscopic method, the author shows that when air saturated with an odoriferous substance, such as pyridine or camphor, is bubbled through a liquid containing a lipoid, such as a suspension of lecithin or of fatty animal tissue in Ringer's solution, more odoriferous substance is adsorbed than when the saturated air passes through water. The bearing of these results on Overton's theory of narcotic action is discussed.

H. W. B.

Relation between Odour and Constitution. H. J. PRINS (*J. Soc. Chem. Ind.*, 1917, **36**, 942—943; from *Perf. and Essent. oil Rec.*, 1917, **8**, 222—223).—Majewski's theory (A., 1902, i, 103) that the odour of substances is due to the presence of 'osmophoric' groups has been modified by Marchand (*Deuts. Parf. Z.*, 1915, 232, 243, 287), who concluded that the non-osmophoric part of the molecule determined the class of odour, whilst its shade or tinge depended on the osmophoric group. It is more correct to regard all groups as osmophoric, but different in strength. Thus the odour of derivatives of benzene is similar because the substituting groups cannot entirely overcome the osmophoric influence of the benzene

molecule. On the other hand, the different odours of octyl alcohol, octaldehyde, and octoic acid demonstrate the weak osmophoric influence of the aliphatic hydrocarbons. Chemically homologous substances have similar odours, for example, octaldehyde, nonaldehyde, and decaldehyde, and octyl, nonyl, and decyl alcohols. If an alteration in the hydrocarbon part of an aromatic substance has a great influence on the chemical character of the strongest osmophoric group, there will be a considerable change in the odour (compare the difference in odour between lauraldehyde and methylnonylacetaldehyde). Double bonds in the neighbourhood of an alcoholic, aldehydic, or carboxylic group have a marked influence on odour (compare decaldehyde with undecenaldehyde, citronellal with citral, α-ionone with β-ionone). Of two changes in the constitution of a compound, the odour will be most affected by that which has the strongest influence on the most powerful osmophoric group. The influence of formic acid preponderates over that of alcohols in the formic esters, the preponderance being least in the formates of strongly osmophoric alcohols, such as borneol and menthol. H. W.

Relation of the Quality of Proteins to Milk Production. III. E. B. HART and G. C. HUMPHREY with BARNETT SURE (*J. Biol. Chem.*, 1917, **31**, 445—460. Compare Hart, Humphrey, and Schaal, A., 1916, i, 771).—Similar experiments to those already described have been carried out with a basal ration containing clover hay instead of corn stover. In these circumstances, positive nitrogen balances were maintained during most of the period of observation (sixteen weeks) with a slow shrinkage in milk volume, but a maintenance of the percentage composition of the milk. The replacement of the corn stover by clover hay therefore increases the efficiency of the protein concentrates added to the basal diet of cows, especially in the case of the gluten feed. H. W. B.

Distribution of the Fatty Acids in the Milk Fat of the Cow and Sheep. CHARLES CROWTHER and ALEXANDER HYND (*Biochem. J.*, 1917, **11**, 139—163).—The amounts of the different fatty acids present in milk or butter-fat are estimated by converting them into methyl esters and then subjecting the mixed esters to fractional distillation. The preparation of the methyl esters is accomplished by heating the fat in ethereal solution with excess of methyl alcohol containing a small proportion of hydrogen chloride. The mixed esters are separated from the neutralised reaction mixture and then fractionally distilled three or four times, in each case under atmospheric pressure until a temperature of 150—160° is reached, and subsequently under diminished pressure. A series of fractions is obtained, each of which contains only two saturated esters and one unsaturated ester, which is found to be methyl oleate in each case. From the iodine absorption and the saponification values of each fraction the weight of each ester contained in it is calculated. By summing up the results for the individual fractions, the weight of each acid in the original weight of fat taken is readily determined. A control using an artificial mixture of the

acids occurring in butter-fat was carried out with satisfactory results. On an average, it is found that the total loss of esters incurred during the whole estimation amounts to less than 1% of the weight of fat taken for analysis.

By the application of this method the fat contained in the "first runnings" of milk from a cow is shown to differ considerably from the fat contained in the "last runnings," or "strippings"; whilst the milk-fat of the cow shows distinct differences from that of the ewe. The average percentage amounts of fatty acids in normal butter-fat are as follows: Butyric, 4·27; hexoic, 1·64; octoic, 1·16; decoic, 1·19; lauric, 5·01; myristic, 16·43; palmitic, 14·83; stearic, 3·40; dihydroxystearic, 0·38; and oleic, 44·42. H. W. B.

Blood Lipoids in Anæmia. W. R. Bloor and D. J. MacPherson (*J. Biol. Chem.*, 1917, **31**, 79—95).—The authors have examined the distribution of the lipoids in the blood of numerous persons suffering from anæmia. As long as the percentage of corpuscles in the blood remains above half the normal value, the percentages of the various lipoids are the same as those associated with healthy blood. When the percentage of corpuscles falls below this limit, the plasma usually contains an excessive amount of fat, whilst there is a decrease in the amounts of cholesterol and lecithin. The corpuscles in nearly all cases have the normal content of lipoids, which indicates that the anæmic condition is not due to an abnormal susceptibility of the corpuscles to hæmolysis. The normal relation between the free and combined cholesterol in the blood plasma is also unaltered in anæmia, which lends no support to the view that anæmia is associated with an abnormally large combination of cholesterol as ester.

The low values for lecithin and the high values for fat which are generally most marked in those cases where the percentage of blood corpuscles is lowest are regarded by the author as due to deficient assimilation of fat in the blood, resulting from the lack of sufficient corpuscles to bring about the change of fat to lecithin, which is believed to be one function of the corpuscles (Bloor, A., 1916, i, 450). The authors direct attention to the low values for cholesterol, which is an antihæmolytic substance, and to the high fat fraction, which suggests the presence of abnormal amounts of hæmolytic substance in the blood in the anæmic condition.

Splenectomy, in anæmic, as in normal cases, is followed by a rise in the percentage of lecithin and fatty acids in the corpuscles and of cholesterol in the plasma. H. W. B.

Effect of Hydrochloric Acid on the Mineral Excretion of Dogs. Raymond L. Stehle (*J. Biol. Chem.*, 1917, **31**, 461—470).—The administration of hydrochloric acid to dogs causes an increased excretion of calcium and magnesium, as well as of sodium and potassium, in the urine and fæces. After two or three days a retention of sodium and potassium occurs, which compensates for the preliminary loss observed. By far the larger proportion of the ingested acid is eliminated in combination with ammonia.

H. W. B.

Diverse Physiological Behaviour of certain Stereoisomeric Alcohols of the Cholesterol Series. A. WINDAUS (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 301—304; from *Chem. Zentr.*, 1917, i, 1017—1018).—It is well known that stereoisomerides may differ in their physiological behaviour, but the chemical processes which are caused by such differences do not appear to have been definitely investigated. Certain alcohols of the cholesterol series, notably β- and ε-cholestanol, are specially adapted for an examination of this question. Experiments have shown that β-cholestanol, like cholesterol, inhibits the hæmolytic action of certain blood poisons, for example, the saponins (digitonin), possessing in this respect approximately the same activity as cholesterol itself. ε-Cholestanol, on the other hand, is far less active than the β-compound, and only shows slight antihæmolytic action towards saponins. Experiments were performed with the following solutions: (*a*) fresh de-fibrinated ox-blood (5 c.c.) diluted with physiological salt solution to 100 c.c.; (*b*) solution of digitonin (1 part) in water (10,000 parts); 1 c.c. of this solution hæmolyses 5 c.c. of diluted ox-blood; (*c*) solution of cholesterol or β- or ε-cholestanol (1 part) in methyl alcohol (200 c.c.). In every case precautions were taken to have the solution containing 0·9% of sodium chloride. The experiments lasted for twenty-four hours, the temperature being 18—20°. Five c.c. of diluted blood showed no hæmolysis with digitonin solution (1·5 c.c.), cholesterol solution (1·5 c.c.), and salt solution (2 c.c.) or with digitonin solution (2 c.c.), cholesterol solution (2 c.c.), and salt solution (1 c.c.). β-Cholestanol showed similar behaviour, whilst, in presence of ε-cholestanol complete hæmolysis occurred. The use of a large excess of the latter compound gradually weakens the action of digitonin, probably owing to absorption. According to Windaus (A., 1909, i, 920), the antipoisonous action of cholesterol towards saponins depends on the formation of an additive compound of cholesterol and digitonin, which is almost inactive physiologically. β-Cholestanol likewise yields additive compounds with digitonin and other saponins, differing thus from the ε-compound (A., 1916, i, 813). The differing physiological behaviour of the stereoisomeric cholesterol alcohols is therefore to be attributed to their ability or inability to form inactive complex compounds. H. W.

Fate of Inositol Administered to Dogs. ISIDOR GREENWALD and MORRIS L. WEISS (*J. Biol. Chem.*, 1917, **31**, 1—14. Compare R. J. Anderson, A., 1916, i, 688).—Subcutaneous injection of inositol into normal and phloridzinised dogs in a fasting condition is accompanied by a slight increase in the value of the urinary D/N ratio. Only small amounts of unchanged inositol appear in the urine. Corresponding with the increased excretion of dextrose, there is a slight decrease in the elimination of acetone and β-hydroxybutyric acid. It appears, therefore, that inositol is slowly converted into dextrose in the animal organism.

H. W. B.

Physiological Behaviour of Raffinose. SHIGENOBU KURIYAMA and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1917, **31**, 125—147).—Raffinose is devoid of nutritional value until after it has been hydrolysed. After parenteral injection into rabbits in doses of of from 2 to 3 grams per kilo. of body-weight, 88% of the injected raffinose is recovered unchanged in the urine. When it is introduced directly into a loop of the small intestine of a dog it is unchanged, and can be recovered almost quantitatively after two hours. Human saliva, the bile, pancreas, liver, and mucous membranes of the small and large intestines of the dog and rabbit do not contain raffinase; the gastric juice exerts a slight hydrolytic action under certain conditions on raffinose.

When raffinose is fed to animals, it is hydrolysed in the large intestine by bacteria. The same effect is observed when the raffinose is introduced directly into the large intestine, and the resulting compounds are utilised in the body. It is probable that bacteria capable of hydrolysing raffinose occur most frequently in the large intestines of species of animals which consume foods containing raffinose.

Raffinase (from yeast) exerts its maximum activity in a medium of which the hydrogen-ion concentration (pH) lies between 3·8 and 5·4. H. W. B.

The Toxicological and Urological Characterisation of 2:4-Dinitrophenol. L. LUTZ and G. BAUME (*J. Pharm. Chim.*, 1917, [vii], **16**, 61—62).—2:4-Dinitrophenol, of which the toxicity coefficient is above 0·2 gram per kilo. of body-weight of the animal, passes through the animal unchanged, and is found in the urine. For its detection, the organic matter is destroyed by sulphuric acid, and the solution boiled to eliminate formaldehyde. The dinitrophenol is extracted by light petroleum, the solvent is evaporated, and the residue dissolved in water. The presence of dinitrophenol is shown by the formation of a red or pale pink coloration when this solution is boiled with a freshly prepared solution of potassium cyanide, or by the formation of an orange-red ring when a solution of ammonium sulphide is added to the aqueous solution of the dinitrophenol, which has been mixed with its own volume of aqueous sodium hydroxide. W. G.

Intravenous Injections of β-Hydroxybutyric and Acetoacetic Acids. RUSSELL M. WILDER (*J. Biol. Chem.*, 1917, **31**, 59—65).—The intravenous injection of lævorotatory sodium β-hydroxybutyrate into dogs does not lead to the appearance of β-hydroxybutyric acid in the urine until the rate of injection reaches 0·4 gram per kilo. of body-weight per hour. Sodium acetoacetate appears in the urine when the rate of its injection into the blood is 0·2 gram per kilo. of body-weight per hour. When the rate of injection of sodium acetoacetate is increased to 0·4 gram per kilo. of body-weight per hour, β-hydroxybutyric acid is eliminated in the urine. The author draws the conclusion that, under the conditions of the experiment, the acetoacetic acid is

converted almost quantitatively into β-hydroxybutyric acid. No evidence of the reverse change was obtained. H. W. B.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. I. Toxicity. A. L. Walters and E. W. Koch (*J. Pharm. Expt. Ther.*, 1917, **10**, 73—81. Compare Karrer, A., 1916, i, 833, and Meader, A., 1916, i, 834).—The authors have measured the relative toxicity of the methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, *tert.*-butyl, amyl, *iso*amyl, and allyl ethers of cephaeline. The substitution of the methyl group in emetine (cephaeline methyl ether) by radicles of the higher homologous alcohols markedly decreases the toxicity for rats, guinea-pigs, and rabbits. The *iso*amyl ether is the least toxic of the series, having about one-fifth the toxicity of emetine when given subcutaneously.

Emetine is not a very toxic alkaloid when given in a single dose, but is dangerous when given repeatedly in small doses over a considerable period of time. H. W. B.

Alleged Antineuritic Properties of 2-Hydroxypyridine and Adenine. Arthur Harden and Sylvester Solomon Zilva (*Biochem. J.*, 1917, **11**, 172—179. Compare Williams, A., 1916, i, 697, and this vol., i, 353).—The authors confirm the existence of 2-hydroxypyridine in two crystalline forms, but fail to observe any curative action of either form on polyneuritic pigeons. Similar negative results are recorded for adenine (compare Williams, *loc. cit.*).

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Vital Stains. WERNER SCHULEMANN (*Ber.*, 1917, **50**, 772—774; see also this vol., i, 369).—Polemical in reply to Skraup (this vol., i, 369; A., 1916, i, 869). D. F. T.

Bacillus paralacticus. F. DUCHÁČEK (*Biochem. Zeitsch.*, 1917, **82**, 31—47).—*B. paralacticus* was isolated from lactobacilline. It produces in milk 0·6—0·7% lactic acid, whereas *B. bulgaricus* produces under the same conditions 2·3—2·5%. The whole amount of the fermented sugar in the milk is converted into lactic acid. If the bacillus acts in the presence of the neutralised medium (in the presence of calcium carbonate), 50% of the sugar can be fermented in four months. Under the same conditions, *B. bulgaricus* can cause fermentation of the whole of the sugar within ten to fourteen days. The reason of this difference is that the coagulum produced in the fermentation is sufficiently acid to inhibit the action of the former species of bacillus. The best

medium for the growth of *B. paralacticus* is peptonised malt extract containing a suitable sugar. A further distinction between *B. bulgaricus* and *B. paralacticus* is that the latter produces *r*-lactic acid, whereas the former produces an inactive acid. About 4·6% of the acid produced is in both cases acetic acid. S. B. S.

Colour Changes Produced by Two Groups of Bacteria on Caseinogen and certain Amino-acids. ELFRIDA CONSTANCE VICTORIA CORNISH and ROBERT STENHOUSE WILLIAMS (*Biochem. J.*, 1917, **11**, 180—187).—Discoloured Stilton cheese contains a very large number of micro-organisms belonging to many different groups. Similar micro-organisms are present in the milk from which the cheese is made, and also in the water supplies of the farms from which the milk is obtained. The authors have arbitrarily selected certain members of two of these groups, and have studied their action on caseinogen and amino-acids from the point of view of colour production.

The two groups selected were the *B. proteus* group and a group of bacilli which were Gram-negative and produced an alkaline reaction in solutions of various sugars, alcohols, etc., into which they were inoculated. The results show that the members of the former group produced a well-marked amber colour in media containing tryptophan, whilst those of the latter group caused a yellow colour to appear in media containing tryptophan and a definite brown colour in caseinogen solutions. H. W. B.

The Extraction of Different Preparations of Dried Yeast. EDUARD BUCHNER and SIEGFRIED SKRAUP (*Biochem. Zeitsch.*, 1917, **82**, 107—133).—From acetone-treated yeast, the zymase, protein, and endotryptase can only be extracted by water after grinding. This is not the case, however, with air-dried yeast prepared by Lebedev's process. From such preparations, the zymase, etc., are readily extracted by water, and previous grinding does not improve the extracts. The authors discuss in some detail the structure of the yeast and the theories put forward to explain the relationships between the ferments and the protoplasm. S. B. S.

The Action of Toluene on Fermentation Processes. EDUARD BUCHNER and SIEGFRIED SKRAUP (*Biochem. Zeitsch.*, 1917, **82**, 134—140).—Toluene has practically no influence on the rate of fermentation by acetone preparations of yeast. This is not in accordance with the results of Euler and Kullberg. On repeating their experiments (at 31°) with Lebedev preparations or maceration juice made therefrom, it was found that toluene did inhibit fermentation, as these authors observed. The inhibition took place, however, only in the earlier stages of the fermentation; in later stages this could not be observed; in fact, after the first inhibition, the rate increased somewhat in the presence of toluene.
S. B. S.

Influence of Available Carbohydrates on Ammonia Accumulation by Micro-organisms. SELMAN A. WAKSMAN (*J. Amer. Chem. Soc.*, 1917, **39**, 1503—1512).—The growth of

Aspergillus niger and *Citromyces glaber* in a peptone medium, with and without added sucrose, has been studied. It is found that, in the absence of sugar, the organisms grow slowly, but that ammonia accumulates rapidly, whereas in the presence of sugar, the weight of mycelium increases rapidly until auto-digestion sets in, the amount of ammonia produced is very small as long as sufficient carbohydrate remains, but the peptone disappears rapidly. In the absence of sugar, therefore, the fungus attacks the protein for its fuel and carbon requirements, and so sets free an excess of nitrogen as waste ammonia. If sugar is added, the protein is almost entirely used in producing fungus mycelium, no waste ammonia being left over, and the carbohydrate is drawn on for fuel.

The results have an obvious bearing on some soil problems, particularly the ill-effects of adding available carbohydrates to the soil. The soil bacteria and fungi make a preferential attack on the carbohydrate and release very little surplus nitrogen as ammonia from the proteins. However, the judicious application of small quantities of a carbohydrate to the soil might be advantageous in stimulating the early development of more micro-organisms. J. C. W.

Citric Acid Fermentation of Aspergillus niger. JAMES N. CURRIE (*J. Biol. Chem.*, 1917, **31**, 15—37).—According to the author, the fermentation of a sugar by *Aspergillus niger* may be regarded as an oxidation proceeding in three stages, producing citric acid, oxalic acid, and carbon dioxide respectively. He has attempted, therefore, to ascertain the best conditions for accelerating the first and depressing the last two stages in the process. By a judicious selection of cultures and conditions, the production of citric acid can be varied from none at all to more than 50% of the sugar consumed.

The conditions especially favourable for the production of citric acid are a high concentration of sugar and a low concentration of nitrogen, the nitrogen being supplied as ammonium salts rather than as nitrates. When nitrogen is supplied in the form of ammonium salts or as asparagine, iron does not stimulate the metabolic processes in any way, but when the supply of nitrogen is in the form of nitrates, iron has a marked stimulating effect, especially noticeable in the increased production of carbon dioxide.

The addition of calcium carbonate to reduce the growing acidity of the culture medium is deprecated; indeed, the fermentation is found to proceed best in a fairly acid medium. The most suitable medium for conducting the citric acid fermentation by *Aspergillus niger* contains 12·5% to 15% of sucrose, 0·2% to 0·25% of ammonium nitrate, 0·075% to 0·1% of potassium dihydrogen phosphate, 0·02% to 0·025% of crystallised magnesium sulphate, and 0·4 to 0·5 c.c. of $N/5$-hydrochloric acid, corresponding with a pH of 3·5 to 3·4. The addition of the acid greatly reduces the dangers of infection with organisms which might interfere with the citric acid fermentation. Under the prescribed conditions, the amount

of citric acid produced reaches its maximum about the eighth day, and the medium then contains about 10% of citric acid.

Variability in the fermenting power of cultures which cannot be distinguished on morphological grounds is often observed, and good results can only be obtained by careful selection of the moulds to be employed. When the fermentation proceeds properly, the mould does not form spores, but remains quite white. H. W. B.

The Action of Soaps on the Fermentative Degradation of Starch and Glycogen. SIEGMUND KENDE (*Biochem. Zeitsch.*, 1917, **82**, 9—30).—The soaps of the higher fatty acids inhibit the degradation by diastase of starch and glycogen. This action differs from the ordinary action of ferment inhibitors in that the soap does not act directly on the enzyme, but on the substrate, with which it forms what is apparently an adsorption compound. Soaps will not inhibit, for example, the degradation of dextrins by diastase. The inhibitory action is annihilated by the presence of small quantities of acids. The results were obtained by the author as a result of investigations of the inhibitory action of the expressed juice of pancreas on the action of diastase, which he succeeded in proving to be due to the presence of soaps contained in such juice. He discusses in some detail the physiological function of the soaps, especially in the relationship to the glycogen fixation in the liver. S. B. S.

Nitrate Assimilation. O. LOEW (*Ber.*, 1917, **50**, 909—910).—A reply to Baudisch (this vol., i, 434). A reaffirmation that nitrate assimilation is not a photochemical process (see A., 1912, ii, 797). J. C. W.

The Development of the Typical Glucosides of the Leaf in Germinating and Growing Digitalis Plants. WALTHER STRAUB (*Biochem. Zeitsch.*, 1917, **82**, 48—59).—The amount of the glucosides in different stages of the growth of the plant was estimated by a pharmacological method (by ascertaining the number of lethal doses for a frog in different fractions). The glucosides in question are digitalinum verum and digitalein, which are soluble in water, and both of which are found in the seeds, and digitoxin, which is insoluble in water, but soluble in chloroform, and "gitalin," which is soluble in chloroform and cold water, which are found in the leaves. Digitalein also occurs in the leaves. As a result of pharmacological tests of the fractions obtained from plants in various stages of the growth, a very approximate quantitative estimation of these alkaloids could be made. It was found that the glucosides of the seeds are not reserve material, but disappear during germination, and are stored in the leaves, in which organs they do not increase further in quantity. The glucosides proper of the leaves make their first appearance in the earliest foliage leaves and continue to increase in quantity until they form 1% of the dried matter. Reasons are given for sup-

posing that they are only waste products of the metabolism of plant growth. S. B. S.

Function of Calcium in the Nutrition of Garden Pea Seedlings with Ammonium Salts. V. A. MORSOV (*Papers from Lab. of Prof. Prianichnikov, Moscow Institute of Agriculture*, 1916, **10**, 391—395; *Bull. Agric. Intell.*, 1917, **8**, 214—216; from *J. Soc. Chem. Ind.*, 1917, **36**, 898).—In the assimilation of ammonium salts by plants, the base is absorbed and the acid left; this acid requires to be neutralised if continued assimilation is to go on. Experiments were made with sprouted seeds of the garden pea grown in solutions of ammonium sulphate alone, ammonium sulphate and calcium carbonate, and ammonium sulphate and ferric hydroxide. The best development of the seedlings occurred with the solution containing calcium carbonate, the second best with ferric hydroxide, whilst that with ammonium sulphate alone was poorer than with distilled water. The greatest accumulation of total nitrogen and asparagine nitrogen in the seedling also occurred with calcium carbonate followed by ferric hydroxide, whilst the ammoniacal nitrogen was least with calcium carbonate. Thus calcium carbonate does not act merely as a neutralising agent, but the calcium present also exerts its own specific nutritive influence. T. S. P.

Rôle of Ammonia in the Metabolism of Nitrogenous Substances in Plants. D. N. PRIANICHNIKOV (*Collected Papers of Agronom. Inst. of Moscow*, 1916, **10**, 1—24; *Bull. Agric. Intell.*, 1917, **8**, 204—211; from *J. Soc. Chem. Ind.*, 1917, **36**, 898).—In the life of the higher plants, ammonia plays an important part as the starting point for the synthesis of protein and as an end-product in the oxidation of nitrogenous substances. It does not, however, accumulate as such, but is converted into asparagine.

Plants may be divided into three types, according to the facility with which they accomplish this synthesis of asparagine: (*a*) Plants which readily absorb ammonia from solution and convert it into asparagine. *Hordeum sativum* (barley), *Zea mais* (maize), and *Cucurbita pepo* (pumpkin) belong to this group. (*b*) Plants in which the absorption of ammonia is very feeble, and the presence of ammonia in the culture solution retards the oxidation of nitrogenous substances. The absorption of ammonia can be increased by adding calcium carbonate to the culture solution. *Pisum sativum* (pea) and *Vicia sativa* (vetch) are plants of this type. (*c*) Plants in which the presence of ammonia in the culture solution prevents the conversion of ammonia into asparagine. The addition of calcium carbonate has no effect in these cases. The yellow lupin (*Lupinus luteus*) is an example of this type.
T. S. P.

Various Modes of Combination of Methyl Alcohol in Plants. Estimation of Pectin-and Lignin-Methyl Alcohol in Roots. TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, **8**, 1—29; from *Chem. Zentr.*, 1917, i, 1154—1155).—In addition to

pectin, the majority of plants contain other methoxy-compounds in which the methoxy-group is more firmly combined and is not eliminated by sodium hydroxide. In such cases, methyl ethers are obviously present. Since Zeisel's process is somewhat cumbersome and does not allow a distinction between the methyl groups present in ester or ether groups, the author has modified his previous process (A., 1916, ii, 351). This also presents the advantage of only indicating methyl groups, whilst, by Zeisel's methods, other alkyl groups are also eliminated. The lignocelluloses, and also suberin, contain firmly-bound methyl alcohol.

The literature of the lignocelluloses is reviewed, and the analyses recorded therein lead the author to propose the formula $C_{22}H_{19}O_9Me_2$ for the hypothetical lignin of wood. In accord with König and Rump, the author includes under the term 'lignin' those non-volatile, methoxy-compounds of plants which are insoluble in alcohol and ether and do not yield methyl alcohol when treated with sodium hydroxide, but do so with concentrated sulphuric acid. Since the methoxy-content of these substances is variable and generally unknown, and the compounds can only be recognised by their methoxy-content, the author prefers to consider them as 'lignin–methyl alcohol,' and not as 'lignin.' The assumption of König and Rump (*Zeitsch. Nahr. Genussm.*, **18**, 177), that cellulose and lignin are only intimately associated and not chemically united in the crude fibres, is not justified by the evidence they adduce.

In connexion with the form of occurrence of methyl alcohol in plants, the author has examined pine wood, cork, normal and brown hay, roots and their adulterants, cocoa and cocoa shells. It is found that the pectin of wood is not identical with that of fruit, since it is insoluble in water and not dissolved when heated under pressure with organic acids. Cork contains several methoxylated acids and a certain proportion of lignin, the methyl alcohol of which constitutes about 25% of the total methyl alcohol. In the fermentation of brown hay, methyl alcohol is eliminated from the pectin and partly oxidised to formic acid; simultaneously, an increase occurs in the lignin–methyl alcohol.

For the estimation of total methyl alcohol, the finely ground sample, freed from fat if necessary (0·2—0·5 gram), is heated to gentle ebullition for ten minutes with sulphuric acid (72%, 15 c.c.). After cooling, water (25 c.c.) is added, and the mixture is distilled until 25 c.c. have been collected. The distillate is made alkaline with sodium hydroxide, and again distilled until 16·2 c.c. have passed over. With substances of low methoxyl content, two further distillations are performed, in which 10 c.c. and 6 c.c. respectively are collected. The final distillate is weighed and colorimetrically investigated, as previously described. The lignin–methyl alcohol is deduced from the differences between the values for the total and pectin–methyl alcohol. When very small quantities of lignin are present, it is advisable to estimate both forms in the same sample; the distillation residue obtained after estimation of the pectin is filtered, washed with hot water, alcohol, and ether, dried, and distilled with sulphuric acid. H. W.

The Biochemical Phenomena of Oxido-reduction. JACQUES EMIL ABELOUS and JULES ALOY (*Compt. rend.*, 1917, **165**, 270—272).—The authors have repeated Bach's work (compare this vol., i, 375) on the reducing enzyme present in milk and potatoes, and find that a large number of substances, in addition to aldehydes, act as co-enzymes. Such substances are amines, compounds with heterocyclic rings such as quinoline, terpenes, and even inorganic compounds such as manganous salts. The presence of a substance readily oxidised is sufficient for the reduction of nitrates or chlorates to occur when added to fresh milk. In the case of the precipitate obtained from potato juice on the addition of alcohol, the reducing action of its enzyme is apparently favoured by the presence of starch and amylase. W. G.

The Carbohydrates of Lichens. B. TOLLENS (*J. pr. Chem.*, 1917, [ii], **95**, 132).—Attention is directed to a paper by Ulander and Tollens (A., 1906, ii, 193) on this subject. D. F. T.

Analysis of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1917, **39**, 1470—1476).—An analysis of the pollen of ragweed (*Ambrosia artemisifolia*) has been undertaken, as it is regarded in America as the chief cause of "hay fever" or autumnal catarrh. The grain is spherical, of an average volume of 9^{-7} cubic mm., and the cell-wall constitutes about 65% of the whole. The following composition was determined: moisture, 5·3%; crude fibre, 12·2%; pentosans, 7·3%; ash, 5·4%; dextrin, 2·1%; protein, 24·4%; soluble in alcohol, 42·9%, consisting of fat, 10·8%, lecithin, 0·75%, sucrose, 0·4%, dextrose, 1·6%, resin, 17·4%, and a nitrogenous base. Of the protein, about 7·5% could not be extracted, 6·75% was soluble in alkali, and about 5% could be extracted by 10% salt solution. Ragweed pollen contains much less protein, especially albumin and globulin, than rye pollen. Two hay fever subjects were found to show characteristic ophthalmic disturbances with amounts of the protein of the order of 1^{-6} to 5^{-6} grams, that is, about the same as the minimum amount of rye pollen protein. J. C. W.

Action of Coal Gas on Plants. III. Action of Coal Gas, whilst passing through Soil or Water, on Roots and Leafy Branches. C. WEHMER (*Ber. Deut. bot. Ges.*, 1917, **35**, 403—410. Compare this vol., i, 531).—In the present series of experiments, young annuals, such as cress, grasses, or beans, were grown in culture solutions through which coal gas was slowly bubbled, or in pots so arranged that gas could be led into the soil from above or below. In addition, leafy shoots of the lime, elder, privet, ilex, *Philadelphus*, and various conifers were kept under observation in culture solutions treated with gas.

It appears that undiluted coal gas is highly toxic for the roots of plants, but that the constituents which dissolve in water are not so acutely dangerous. The effect on young cress, for example, is much more striking if the gas is led up through the soil than it is if the gas is just led into the top layers.

The experiments on leafy shoots show that the ill-effects of coal gas on the upper parts of a plant are not always conditioned by damage to the roots, as some have supposed. Still, the effects of the ascent of water charged with the gas into the shoots vary remarkably from part to part of the shoot and from plant to plant. With the exception of the yew, most conifers are highly resistant, but the usual effect is an early shedding of the leaves, the rind and buds remaining practically unhurt. The unfolding of the buds on horse chestnut shoots is quite undisturbed in water charged with gas.

It is just as difficult to say which of the water-soluble constituents of coal gas is particularly toxic, that is, in the concentration in which it occurs in the gas, as it was in the earlier cases of the undiluted gas itself. In this connexion it is now reported that an atmosphere containing 1% of hydrogen sulphide is fatal to the seed or seedlings of cress, but that in the concentration 0·03%, that is, more than is commonly found in coal gas, this "poison" is distinctly beneficial to the germination of cress. J. C. W.

Sensitiveness of Plants to Poisoning with Coal Gas. SARAH L. DOUBT (*Pharm. J.*, 1917, **99**, 111; from *Bot. Gaz.*, 1917, **63**, 209—224).—The increasing loss of plants in greenhouses and of trees in the streets of American towns is attributed largely to coal gas poisoning. On account of their sensitiveness in this respect, tomato plants, *Salvia splendens*, *Mimosa pudica*, *Ricinus communis*, *Datura stramonium*, and *Dianthus caryophyllatus* are suitable as test plants. With all these except the carnation, the presence of 50 parts of coal gas per million of air causes epinastic growth of petioles; the flower buds of carnations wither in this degree of pollution. A mixture of coal gas and air in the proportion of 1 : 1000 causes the leaves of the above plants to fall off, as well as those of *Coleus* and of *Hibiscus rosa sinensis*. Ethylene exerts a similar effect. The following plants are stated to be unaffected by a concentration not exceeding 1 : 400 of coal gas in air, which is the lowest concentration that can be detected by smell: *Calladium esculentum*, *Lupinus perennis*, *Eriobotyra japonica*, *Phoenix canariensis*, *Conocephalus sp.*, *Canna*, *Achyranthes lindini*, *Alternanthera sp.*, *Cytisus canariensis*, and species of *Polypodium*. Many trees, including elder, ash, lime, and catalpa, are very sensitive to gas escaping into the soil. The above-named gas-sensitive plants may be employed for the detection of slight contamination of the air by coal gas. H. B. H.

The Effect of Hydrogen and Hydroxyl-ion Concentration on the Growth of Barley Seedlings. D. R. HOAGLAND (*Soil Sci.*, 1917, **3**, 547—560).—Barley seedlings were grown in partial nutrient solutions, having the same osmotic pressure but a considerable range of hydrogen- and hydroxyl-ion concentrations, this being obtained by the use of suitable mixtures of the three potassium phosphates. The hydrogen-ion concentrations were determined by hydrogen electrode measurements (compare Clark and Lubs,

A., 1916, ii, 513). The hydroxyl ion in such solutions was more toxic than the hydrogen ion for similar divergences from the neutral point. Solutions having a concentration of hydroxyl ion greater than $1 \cdot 8 \times 10^{-6}$ were distinctly injurious, and greater than $2 \cdot 5 \times 10^{-5}$ were very toxic. A concentration of hydrogen ion of approximately $0 \cdot 7 \times 10^{-5}$ was favourable to growth and produced no injury, but a concentration of $0 \cdot 3 \times 10^{-3}$ was very toxic. Microscopic examination showed injury to the root tips, and in many cases the leaves also gave evidence of toxicity. There was found to be a change in the hydrogen-ion concentration of the culture solutions after one or more days' growth. In general, the alkaline solutions decreased markedly in hydroxyl-ion concentration, acid solutions decreased slightly in hydrogen-ion concentration, and neutral solutions remained practically constant. W. G.

Does the Addition of Sulphuric Acid to the Soil Affect the Growth of the Beet? K. ANDRLÍK (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 685—688).—Instead of adding soluble nutrients to the soil, the author has thought it to be worth while to try the effect of applying cheap chemicals, like the mineral acids, to render more of the natural constituents of the soil available to the plant. He has compared the growth of sugar beet on field plots sprinkled before seed-time with dilute sulphuric acid (2—4 kilos. per acre) and on untreated plots, and finds indications that the weights of root and leaves are less, but the quantity and quality of the sugar slightly greater on the treated soil. J. C. W.

The White Turbidity of Wines. W. T. BARAGIOLA (*Zeitsch. Nähr. Genussm.*, 1917, **33**, 513—520. Compare this vol., i, 373, 374).—The white turbidity which sometimes forms in wines is due to precipitation of ferric phosphate. The remedy is to oxidise the ferrous compounds by aeration and then to clarify the wine with gelatin. Sulphurous acid may be added to prevent further oxidation of ferrous compounds, but the addition of this acid is useless when the turbidity has once formed. W. P. S.

Distribution of Nitrogen in Beer. JOHN SMITH SHARPE (*Biochem. J.*, 1917, **11**, 101—111).—The author has estimated the proportion of total nitrogen in light and strong beers, ales, and porter, combined as protein, amino-acid, and purine respectively. The results show that the protein nitrogen constitutes from 13·2% to 37% of the total nitrogen, which indicates that the amount of protein in beers varies from 0·038 to 0·185%. The amino-acid nitrogen varies from 25% to 46%, and the purine nitrogen from 25·8% to 52·4% of the total nitrogen, the former being present in beer to the amount of from 0·014% to 0·040%, and the latter from 0·010% to 0·039%. A small proportion of the nitrogen is combined in the form of an alkaloid resembling coniine (Chapman, T., 1914, **105**, 1895) and a still smaller amount as a basic substance, which may be betaine. The total nitrogen in the beers analysed varied from 0·039% to 0·113%. H. W. B.

The Soil and Soil-solution. OTTO NOLTE (*J. Landw.*, 1917, **65**, 1—66).—The author develops theoretical considerations concerning the soil and the liquid present in it on the basis of the law of mass action, and it is shown that an important part is played by the displacement of the chemical equilibrium in the soil as a result of the influence of the climate and of the actions of plants, animals, etc. T. H. P.

Action of Frost on the Soil. OTTO NOLTE and ERNA HAHN (*J. Landw.*, 1917, **65**, 75—81).—Frost opens the texture of the soil in consequence of the expansion of the water present, and also, since it removes solvent in a solid state from the system, causes displacement of the equilibrium, the salts undergoing concentration or even precipitation. This action affects first those substances occurring in colloidal solution or in suspension. That such loosening effects soon vanish when the ground thaws, owing to the interstitial spaces becoming filled with water and particles of soil, is shown by successive freezing and thawing of an aqueous suspension of ultramarine particles of uniform size; each freezing increases the extent to which the particles become aggregated. T. H. P.

Soil Colloids. II. Influence of Colloids on Electrical Conductivity of Salts. M. I. WOLKOFF (*Soil Sci.*, 1917, **3**, 423—430. Compare A., 1916, i, 784).—The inorganic colloidal particles, as found in clay, particularly the colloidal gels, reduce the electrical conductivity of solutions of salts, the interference being due possibly either to the fact that the colloidal particles, moving comparatively slowly, interfere with the passage of the free ions, or to the change of the structure of the gel at the point of coagulation, resulting in an increase in the adsorptive capacity of colloids. The adsorption of electrolytes by the gel increases with the increase of the electrolyte present for coagulation. The separation of colloids from crystalloids can be carried out by coagulation with certain electrolytes provided that only a minimum amount of electrolyte is used for complete coagulation. W. G.

The Action of Solutions of Ammonium Sulphate on Muscovite. R. F. GARDINER and EDMUND C. SHOREY (*J. Ind. Eng. Chem.*, 1917, **9**, 589—590).—A statement of the results of preliminary tests showing that mica powder, generally considered one of the most stable of soil minerals, is attacked to a notable extent by dilute aqueous ammonium sulphate, approximately 20% of the potassium present being removed by contact with a 0·5—1% solution for twenty-four hours at 20°. D. F. T.

The Effect of Ammonium Sulphate on Soil Acidity. F. E. ALLISON and R. C. COOK (*Soil Sci.*, 1917, **3**, 507—512).—Pot experiments have been carried out with different soils, varying in texture from a sand to a clay, to test the effect of the repeated application of ammonium sulphate to the soil on the soil acidity. In one series of experiments the soil was left fallow and in the other a crop of buckwheat was taken every three months.

Having regard to the fact that these were only single pot trials, the results show that, where no nitrogenous fertiliser was applied, the increase in acidity of each of the five soils during the year was practically the same, whether the soil carried a crop or was kept fallow. The presence of ammonium sulphate caused an increase in acidity considerably higher than in the control pots. On the average, the increase in acidity in these soils corresponded with about 3·6 kilos. of calcium oxide for every 4·5 kilos. of ammonium sulphate applied. W. G.

Adsorption of Ammonium Sulphate by Soils and Quartz Sand. M. I. Wolkoff (*Soil Sci.*, 1917, **3**, 561—564).—A brief outline of work to be published in greater detail elsewhere. In the case of soils, the results show that, in general, with increase in concentration of the ammonium sulphate solution the percentage adsorption decreases, whilst the total amount of salt going out of solution increases. Quartz sand does not, however, entirely follow this general rule. On addition to the sand, the concentration of the salt solution apparently becomes greater. This is most pronounced in coarse sand, and diminishes as the fineness of the sand increases. The effect is more noticeable the more concentrated is the salt solution used, and when the dilution reaches a certain point for a given sand, then it follows the general rule given for soils. W. G.

Effect of Different Salts on the Formation of Ammonia in Soil. George P. Koch (*J. Biol. Chem.*, 1917, **31**, 411—413).—The presence of small amounts of calcium dihydrogen phosphate increases the production of ammonia from dried blood in soil, whilst magnesium and potassium sulphates, singly or in combination, inhibit it. The toxicity of the magnesium and potassium salts is readily removed by the addition of a sufficient proportion of the calcium salt. H. W. B.

Isolation of Cyanuric Acid from Soil. Louis E. Wise and E. H. Walters (*J. Agric. Research*, 1917, **10**, 85—91).—Cyanuric acid has been isolated from an Indiana soil by extraction with dilute sodium hydroxide, acidification of the extract, and successive precipitation of the cyanuric acid as its mercury and lead salts. It was distinguished from tetracarbonimide by molecular weight determination and by analysis of its double silver–ammonium derivative. It was found to be present to the extent of 6·5 parts per million. The authors now find that the tetracarbonimide stated previously (compare A., 1915, i, 1092) to have been isolated from a loam soil was really cyanuric acid. W. G.

Soil Constituents which Inhibit the Action of Plant Toxins. E. Truog and J. Sykora (*Soil Sci.*, 1917, **3**, 333—352).—In order to determine whether the inhibitive effect of certain soils to plant toxins was due to chemical or to physical factors, a series of pot cultures was carried out in which the physical character of the culture medium was controlled by using either

pure quartz sand or sand mixed with quartz flour or kaolin, whilst its chemical character was varied by the presence or absence of calcium carbonate. All pots received nutrient salts, and in addition the toxic substance under investigation. The test plants were wheat seedlings in all cases.

When copper sulphate was employed as the toxic agent, the increased soil surface obtained by the use of quartz flour and kaolin seemed to have a slight beneficial effect, but this was very small as compared with the effect of calcium carbonate, which completely neutralised any deleterious action of either copper sulphate or copper nitrate. With sodium arsenate, the wheat plants did better when the sand was mixed with quartz flour, but as this effect did not extend to the kaolin pots, it appeared probable that the improved growth was not due to the physical character of the quartz flour, but to certain impurities which it contained and which acted as catalytic agents in the oxidation of sodium arsenate; calcium carbonate was practically ineffectual. With guanidine carbonate, the presence of kaolin had a markedly beneficial effect on growth, but quartz flour had none, and the addition of calcium carbonate was actually deleterious. Assuming that kaolin may be regarded as an acid, the author points out that its probable action is to combine with the guanidine, thereby rendering the latter inactive. This hypothesis, which would also explain the ill-effects of calcium carbonate in the experiment, was confirmed by another experiment in which kaolin was replaced by a definitely acid clay soil.

In another set of pot cultures, the artificial soil media were replaced by two natural soils, one a poor acid sand and the other a fertile loam. Vanillin was used as the toxic agent, and the results showed that whereas it had a decidedly depressing influence on growth in the poor sand when neither fertilisers nor lime were added, it had no effect when used on the good soil.

Summarising the results of the investigation, it is clear that chemical factors played an important part in counteracting the effect of plant toxins in the soil. L. M. U.

The Effect of Soil Reaction on the Availability of Ammonium Sulphate. R. C. Cook and F. E. Allison (*Soil Sci.*, 1917, **3**, 487—498).—A study of the effect of the application of increasing amounts of calcium oxide on three types of soil, a sand, a sandy loam, and a silt loam, having lime requirements respectively of 1360 kilos., 1360 kilos., and 1818 kilos. of calcium oxide per acre, either with or without the application of ammonium sulphate. Pot experiments were carried out, the crop grown being buckwheat. Small applications of calcium oxide produced practically as large crop yields as where enough was applied to neutralise the soil or to make it distinctly alkaline, the beneficial effects of calcium oxide on acid soils being more marked on the sandy soils than on the silt loam. On the more acid soils, although the crop was smaller, it usually contained a higher percentage of nitrogen, the recovery of nitrogen, where

applied, being, in many cases, as great from the acid soils as from the alkaline soils. Buckwheat is able to utilise the nitrogen applied as ammonium sulphate, from soils having lime requirements of 1360—1818 kilos. per acre. W. G.

The Significance of Sodium Salts for Plant Growth and the Application of Salt as Manure. E. BLANCK (*Fühling's Landw. Zeit.*, 1916, **65**, 441; from *Bied. Zentr.*, 1917, **46**, 271—272).—A general survey of the present position as to the value of sodium salts for plant nutrition. Sodium is not an indispensable plant constituent, and cannot replace potassium in the true sense of the term. It is stated, however, that a partial replacement is possible, and, in fact, appears to occur.

The value of applications of common salt for certain plants rests on an indirect effect, inasmuch as sodium salts act as ballast and minimise the risk of the plants suffering from "ash starvation." Sodium appears to be especially suitable for this purpose, as it not only facilitates the absorption of potash, but is also of importance for the translocation of the latter constituent in the plant.

Applications of common salt may induce undesirable changes in the physical condition of some soils, whilst in others they ensure a better utilisation of the soil potash compounds. H. B. H.

Gypsum as a Fertiliser. OTTO NOLTE (*J. Landw.*, 1917, **65**, 67—73).—The literature of this subject is discussed, and the following conclusions are drawn. Gypsum acts on the soil by means of both of its constituents, double decomposition occurring with the mineral compounds of the soil. Owing to its ability to undergo hydrolytic decomposition into acid and base, it influences the reaction of the soil especially by virtue of the constituent with the predominating reaction, that is, the sulphuric acid. Consequently, as far as possible, gypsum should not be used with acid and physiologically acid fertilisers, and in particular should never be applied to acid soils. On the other hand, it acts favourably in conjunction with physiologically basic salts, as it removes or weakens the basic reaction resulting from plant growth, and so assists in the retention of a loose texture by the soil. Gypsum may be employed with advantage when there is a shortage of such physiologically active fertilisers as potassium sulphate and chloride, superphosphate, and ammonium sulphate. T. H. P.

Dissolved Oxygen in Rain-water. ERIC HANNAFORD RICHARDS (*J. Agric. Sci.*, 1917, **8**, 331—337).—Rain-water is very nearly saturated with oxygen when its temperature, as collected, is below 15°. During the summer months, when the temperature of the rain is above 15°, the dissolved oxygen is always less than the saturation quantity, sometimes by as much as 25 per cent. With normal clean rain-water there is no absorption of oxygen in twenty-four hours. Rain-water, like tap-water, if it is not shaken can become strongly supersaturated, owing to rise in temperature, without loss of oxygen. W. G.

Organic Chemistry.

Dissociation and Rearrangement of *iso*- and *tert.*-Butyl Bromides in the Gaseous State at High Temperatures, and their Formation from Hydrogen Bromide and *iso*Butene. R. F. BRUNEL (*J. Amer. Chem. Soc.*, 1917, **39**, 1978—2005. Compare A., 1911, i, 413; ii, 974).—An investigation of the equilibrium between *iso*butyl and *tert.*-butyl bromides and their dissociation products, *iso*butene and hydrogen bromide, at 221° and 275°. It is shown how the dissociation constant for the mixture of bromides at equilibrium may be calculated, and from the results of experiments with the vapour of each bromide the average values 0·0490 and 0·00992 (for mols. per litre) are obtained for the temperatures 275° and 221° respectively.

In the dissociation of these bromides and also in their formation from *iso*butene and hydrogen bromide, catalytic influences are active; in the absence of liquid bromide, the hydrocarbon combines only slowly with hydrogen bromide, and under these conditions *iso*butyl bromide is generally formed in addition to the tertiary compound. On the other hand, in the presence of either liquid bromide the combination proceeds much more rapidly, and unexpectedly gives rise only to the tertiary bromide.

From a knowledge of the above dissociation constant at 275°, the assumption that on cooling the equilibrium mixture of vapours yielded by *iso*butyl bromide or *tert.*-butyl bromide to the ordinary temperature the *iso*butene present passes entirely into the *tert.*-butyl compound, and a knowledge of the composition of the condensed liquid, it is calculated that at the temperature stated 80·0% of the undissociated bromide in the equilibrium mixture exists in the form of the tertiary compound. The values for the dissociation constants of the bromides at the two temperatures stated also enables the calculation of the heat of addition of hydrogen bromide to *iso*butene with production of the equilibrium mixture of bromides, the result being 15,886 cal. D. F. T.

The Action of Phosphoryl Chloride on Methyl or Ethyl Alcohol. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **99**, 187—189).—The calculated quantity of the alcohol is added drop by drop to the phosphoryl chloride, cooling in a freezing mixture. When the mixture is gently warmed, hydrogen chloride and methyl or ethyl chloride are evolved. The residue consists of alkyl metaphosphate, part of which is soluble and part insoluble in chloroform, the insoluble ester being probably a polymeride. The action may be represented by the equations: $POCl_3 + 2EtOH = 2HCl + POCl(OEt)_2$; $POCl(OEt)_2 = EtCl + EtPO_3$. C. H. D.

Esterification. IX. The Esterification of Acetic and Propionic Acids by Methyl, Ethyl, Propyl, *iso*Butyl, and *iso*Amyl Mercaptans. EDGAR M. FABER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1917, **39**, 1930—1938. Compare Reid and others, A., 1910, i, 481; 1915, i, 885; this vol., i, 89).—In extension of the earlier researches, it is found that at 200° the limit of esterification for a mercaptan is much lower than that for the corresponding alcohol, the proportions of the reacting substances apparently having little influence on the limit, which is generally attained under ninety-six hours. With increase in molecular weight of the mercaptans there is a gradual reduction in the final quantity of product, and the limits are also found to be somewhat lower for propionic than for acetic acid. The mercaptan esters of higher molecular weight show somewhat greater tendency to decomposition with formation of hydrogen sulphide under the conditions of the experiments. D. F. T.

Method for Fractionating Fats and Oils. ARMIN SEIDENBERG (*J. Ind. Eng. Chem.*, 1917, **9**, 855—858).—The oil or fat is dissolved in a mixture of two or more solvents (for example, ether and alcohol), one or more of which is more volatile and exerts a greater solvent action on the glycerides. This solvent is first removed gradually by aspirating air through the solution, later the remaining solvent is removed in the same way. Owing to the slow decrease in temperature due to the evaporation, and to the gradual removal of the solvents, the various glycerides are precipitated in the order of their solubility. The various fractions are separated by filtration, and each is again treated as described as often as is necessary to obtain a pure product. W. P. S.

Action of Nitric Acid on Castor Oil. R. BRIGHTMAN (*J. Soc. Chem. Ind.*, 1917, **36**, 984—986).—Castor oil reacts very energetically with a mixture of nitric and sulphuric acids; the violence of the action is largely due to the latter acid, and is avoided when it is replaced by glacial acetic acid. The oil is readily nitrated by dilute nitric acid. The nitrated castor oil obtained by the latter method is a reddish-brown, viscid oil with a characteristic odour. It dissolves readily in acetone, ether, alcohol, or acetic acid, but is insoluble in carbon disulphide. It has D about 1·05. It does not decompose at 100°, but slowly darkens when preserved in a warm place.

The usual analytical methods are only applicable with difficulty to the nitrated oil, and it is best characterised by estimating the nitrogen content by Kjeldahl's method. The saponification number varied in a number of samples from 280 to 340; the iodine number was about 4 to 5, but one sample gave 14·9. The iodine number of the fatty acids varied from 18·8 to 25·3. The nitrogen content varied between 2·3 and 3·8%, but was usually about 3%. The percentage of ash was less than 0·05.

Apparently, the nitrated castor oil is formed from castor oil as the result of two simultaneous processes of nitration and oxidation, and thus probably consists of the triglycerides of the nitric ester of

oxidised ricinoleic acid. With this view its nitrogen content is in close agreement. H. W.

Complex Salts. The Preparation of Potassium Iridotrioxalate and the Optical Resolution of the Iridotrioxalates. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1917, [iv], **21**, 157—172).—A more detailed account of work already published (compare A., 1914, i, 1048). W. G.

Constitution of Mono- and Di-acylmalonic Esters, and of Diacetylacetone. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1917, **50**, 929—952).—It is usual to assume that when β-diketones or β-ketonic esters change into enols, the hydrogen of the new hydroxyl group is drawn from the methylene group which is between the carbonyl groups. Brühl, however, showed that ethyl diacetylmalonate corresponds in its optical properties more closely with an enol of the formula $[CH_2{:}C(OH)]_2C(CO_2Et)_2$, and that ethyl acetylmalonate may be represented perhaps by the formula $CH_2{:}C(OH){\cdot}CH(CO_2Et)_2$ (A., 1894, ii, 434). Bielecki and Henri (A., 1914, ii, 319) have also assigned an abnormal constitution, represented by $CH_2Ac{\cdot}C(OH){:}CH_2$, to acetylacetone. The present authors have now examined these compounds, both optically and chemically, and new light is thrown on their constitutions.

CONSTITUTION OF "ETHYL DIACETYLMALONATE."—The objections to Brühl's formula are that it does not explain why the ester is insoluble in alkali hydroxides, does not react with ferric chloride, and readily loses an acetyl residue by hydrolysis. The true explanation is that the compound is really the *O*-acetate of enolic ethyl acetylmalonate [*ethyl β-acetoxyethylidenemalonate*] (1),

$$OAc{\cdot}CMe{:}C(CO_2Et)_2.$$

The best way to prepare the substance is actually by acetylating the monoacetylmalonate in pyridine solution. Furthermore, different products are obtained when ethyl acetylmalonate is propionylated and ethyl propionylmalonate is acetylated, namely, *ethyl β-propoxyethylidenemalonate* (2) and *ethyl β-acetoxypropylidenemalonate* (3) respectively. Similarly, *ethyl β-propoxypropylidenemalonate* (4), $C_2H_5{\cdot}CO_2{\cdot}CEt{:}C(CO_2Et)_2$, may be prepared. These esters are hydrolysed even by phenylhydrazine, the acyl residues being transferred to this base. Finally, compounds of this type contain the grouping $-C{:}C{\cdot}C{:}O$, which is associated with pronounced optical exaltations. The values of the molecular refractions and dispersions actually found are greater than those calculated for such esters with three carbonyl groups and an ethylenic linking by expected amounts.

For comparison, the properties of these esters are tabulated together. Full data are recorded in the original.

Ester.	B.p. 15 mm.	D_4^{20}.	n_D^{20}.	$E\Sigma_\alpha$.	$E\Sigma_D$.	$E\Sigma_\beta-\Sigma_\alpha$.	$E\Sigma_\gamma-\Sigma_\alpha$.
1	154°	1·113	1·4500	+0·58	+0·59	+22%	+20%
2	160	1·097	1·4513	0·49	0·50	21	22
3	156	1·095	1·4506	0·50	0·51	19	20
4	162	1·078	1·4507	0·44	0·44	19	18

Constitution of Ethyl Acetylmalonate.—Ethyl acetylmalonate is best prepared by the action of ethyl chloroformate on ethyl cuproacetoacetate. Its b. p., under 19 mm., fluctuates between 118° and 129°, which may be due to a difference in b. p. between the ketonic and enolic forms.

The optical properties of this ester clearly point to the presence in the molecule of a conjugated system, which is, of course, suggested also by the acylations described above. The ester (5) is, therefore, an enol of the ordinary type, $OH\cdot CMe\colon C(CO_2Et)_2$, and so is ethyl propionylmalonate (6). There is also chemical evidence in support of this. Ethyl sodioacetylmalonate is very indifferent to the action of alkyl haloids, but the small amount of alkyl derivative which is obtained under strenuous conditions can be shown to be an α-alkyl compound. Although ethyl acetylethylmalonate (7),

$$CEtAc(CO_2Et)_2,$$

cannot be obtained readily by ethylating the acetylmalonate, it can by acetylating ethyl ethylmalonate. Furthermore, the same *ethyl α-chloroacetylmalonate* (8), $CClAc(CO_2Et)_2$, is obtained by the action of sulphuryl chloride on free ethyl acetylmalonate, and by the action of chlorine on the copper salt of this ester. Both specimens are alike in physical and optical properties, both are stable towards alkalis, permanganate, and bromine, and both yield a *compound*, probably of the formula $\begin{array}{l} CMe\cdot C(CO_2Et)_2 \\ \| \qquad\; | \\ N\text{---}N\cdot C_6H_4\cdot NO_2 \end{array}$ (silky, orange-coloured needles, m. p. 81°), when treated with *p*-nitrophenylhydrazine. *Ethyl α-bromoacetylmalonate* (9) can also be obtained from the copper salt.

The principal properties of the esters mentioned in this section are given in the following table:

Ester.	B.p. 15/mm.	D^{20}_4.	n^{20}_D.	$E\Sigma_\alpha$.	$E\Sigma_D$.	$E\Sigma_\beta - \Sigma_\alpha$.	$E\Sigma_\gamma - \Sigma_\alpha$.
5	120°	1·100	1·447	+0·95	+0·97	+44%	+46%
6	138	1·076	1·442	0·67	0·67	27	28
7	130	1·054	1·434	0·24	0·23	1	1
8	132	1·187	1·441	0·31	0·30	4	2
9	144	1·388	1·459	0·24	0·23	7	5

Constitution of Acetylacetone.—As against much evidence in support of a formula of the usual type, $COMe\cdot CH\colon CMe\cdot OH$, for acetylacetone, the authors have been unable to find more than one fact on record which would favour the view that the methylene group between the carbonyl groups is intact; thus,

$$COMe\cdot CH_2\cdot C(OH)\colon CH_2.$$

This is the fact that acetylacetone yields hexachloro- and hexabromo-derivatives which readily give trihalogenoacetones, the former being represented, therefore, by the formula $CX_3\cdot CO\cdot CH_2\cdot CO\cdot CX_3$ (Combes, A., 1888, 666). Combes also described, however, a mono- and a di-chloro-derivative of acetylacetone, and it is obvious from their properties that the halogen atoms are attached to the central carbon atom, thus, $COMe\cdot CCl_2\cdot COMe$ (A., 1890, 1394). Further

evidence in support of this view is now adduced, and the mechanism of the chlorination is indicated as follows:

$$\mathrm{COMe{\cdot}CH{:}CMe{\cdot}OH \longrightarrow COMe{\cdot}CHCl{\cdot}CMeCl{\cdot}OH \longrightarrow}$$
$$\mathrm{COMe{\cdot}CHCl{\cdot}COMe \longrightarrow COMe{\cdot}CCl{:}CMe{\cdot}OH \longrightarrow}$$
$$\mathrm{COMe{\cdot}CCl_2{\cdot}CMeCl{\cdot}OH \longrightarrow COMe{\cdot}CCl_2{\cdot}COMe.}$$

It is suggested that the dihalogeno-derivative is formed in this normal way even in the extreme cases, the hexa-derivatives being produced after internal rearrangement.

Chloroacetylacetone, $\mathrm{COMe{\cdot}CCl{:}CMe{\cdot}OH}$, has b. p. 153—154°, D_4^{20} 1·165, n_D^{20} 1·4783, $E\Sigma_\alpha + 1{\cdot}01\%$, $E\Sigma_D + 1{\cdot}08\%$, $E\Sigma_\beta - E\Sigma_\alpha + 86\%$, calculated for the enolic form; dichloroacetylacetone,

$$\mathrm{COMe{\cdot}CCl_2{\cdot}COMe},$$

has b. p. 79°/11 mm., D_4^{20} 1·303, n_D^{20} 1·4574, $E\Sigma_\alpha + 0{\cdot}18\%$, $E\Sigma_D + 0{\cdot}17\%$, $E\Sigma_\beta - E\Sigma_\alpha + 2\%$, $E\Sigma_\gamma - E\Sigma_\alpha + 2\%$, calculated for the ketonic form; *bromoacetylacetone*, $\mathrm{COMe{\cdot}CBr{:}CMe{\cdot}OH}$, has b. p. 96°/13 mm., irritates the eyes, and quickly becomes dark coloured in the air.

Dichloroacetylacetone reacts with *p*-nitrophenylhydrazine hydrochloride to form a compound which may also be prepared by converting acetylacetone into *p*-nitrobenzeneazoacetylacetone (Bülow and Schlotterbeck, A., 1902, i, 649) and treating this with *p*-nitrophenylhydrazine. The compound is, therefore, 4-p-*nitrobenzeneazo*-1-p-*nitrophenyl*-3 : 5-*dimethylpyrazole*,

$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}N}\!<\!\begin{array}{l}\mathrm{N{=\!=}CMe}\\ \mathrm{CMe{:}C{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2}\end{array};$$

it crystallises in orange-coloured needles, m. p. 236—238°.

J. C. W.

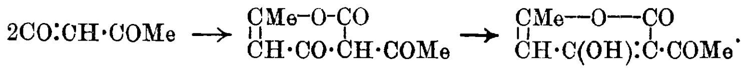
Ketens. XXVI. Ketenmonocarboxylic Esters. H. STAUDINGER and H. BECKER (*Ber.*, 1917, **50**, 1016—1024. Compare A., 1914, i, 285).—Researches on ketens have revealed the facts that mono-substituted ketens are extremely unstable, and that carboxyl groups enhance the tendency of these compounds to form polymerides. It was therefore expected that attempts to isolate ketenmonocarboxylic esters would result in the formation of *cyclo*butane derivatives, thus:

$$\mathrm{2CO_2R{\cdot}CH{:}CO \longrightarrow CO_2R{\cdot}CH}\!<\!\begin{array}{c}\mathrm{CO}\\ \mathrm{CO}\end{array}\!>\!\mathrm{CH{\cdot}CO_2R} \longrightarrow$$
$$\mathrm{CO_2R{\cdot}CH}\!<\!\begin{array}{c}\mathrm{CO{-\!-}}\\ \mathrm{C(OH)}\end{array}\!\geqslant\!\mathrm{C{\cdot}CO_2R \longrightarrow CO_2R{\cdot}C}\!\leqslant\!\begin{array}{c}\mathrm{C(OH)}\\ \mathrm{C(OH)}\end{array}\!\geqslant\!\mathrm{C{\cdot}CO_2R.}$$

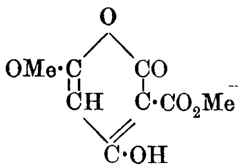
When, in the normal way, methyl and ethyl bromomalonyl chlorides were treated with zinc, practically no definite compounds could be obtained, whilst the alternative method for the production of ketens, namely, the action of quinoline on the ester–chlorides, did not give the hoped-for *cyclo*butane compounds, but pyrone derivatives. The polymerisation of the simple keten takes place in this case according to the scheme:

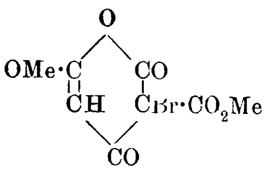
$$\begin{array}{l}\mathrm{OR{\cdot}C{:}O}\\ \quad\;|\\ \mathrm{\;\;\;CH{:}CO}\end{array} + \begin{array}{l}\mathrm{CO}\\ \,\|\\ \mathrm{CH{\cdot}CO_2R}\end{array} = \begin{array}{l}\mathrm{OR{\cdot}C{-}O{-\!-}CO}\\ \quad\;|\qquad\qquad|\\ \mathrm{\;\;\;CH{\cdot}CO{\cdot}CH{\cdot}CO_2R}\end{array}.$$

The pyrone derivatives are quite analogous to dehydracetic acid, the formation of which can likewise be traced to a polymerisation of the unknown acetylketen, thus:



Methyl malonyl chloride, prepared from thionyl chloride and potassium methyl malonate, has b. p. 57—59°, and decomposes to a certain extent into hydrogen chloride and the dimeric keten-carboxylate on distillation. It reacts with aniline to form *methyl malonanilate*, m. p. 42—43°, and with bromine to give *methyl bromomalonyl chloride*, $CO_2Me\cdot CHBr\cdot COCl$, b. p. 90—91°/10 mm. This yields *methyl bromomalonanilate*, m. p. 113—114°, and reacts with zinc to give a very small quantity of a *compound*, $C_8H_8O_6$, m. p. 179—180°, which behaves like a dibasic acid. Methyl malonyl chloride reacts with quinoline to form *methyl* 4-*hydroxy*-6-*methoxy*-1 : 2-*pyrone*-3-*carboxylate* (annexed formula), which crystallises in needles, m. p. 148—150°, and is decomposed by hot water into methyl malonate, malonic and acetic acids, and methyl acetoacetate (*semicarbazone*, m. p. 151—152°). This ester also reacts with ammonia to form malonamide, with aniline to give malonanilide, and with bromine to give the *compound* (annexed formula), decomp. 180—185°.





Ethyl malonyl chloride, b. p. 63—64°/10 mm., may be converted into *ethyl malon*-p-*toluidate*, m. p. 83°, *ethyl bromomalonyl chloride*, b. p. 88—90°/10 mm., *ethyl bromomalonanilate*,

$$CO_2Et\cdot CHBr\cdot CO\cdot NHPh,$$

m. p. 94°, and also *ethyl* 4-*hydroxy*-6-*ethoxy*-1 : 2-*pyrone*-3-*carboxylate*, m. p. 85—86°. J. C. W.

Ketens. XXVII. Ethyl Ketendicarboxylate and Methyl Phenylketencarboxylate. H. STAUDINGER and H. HIRZEL (*Ber.*, 1917, **50**, 1024—1035. Compare this vol., i, 178).—The three ketencarboxylates, ethyl ethylketencarboxylate (A., 1910, i, 89), ethyl ketendicarboxylate, and methyl phenylketencarboxylate, have many unexpected properties. In the first place, they are much paler in colour than the corresponding simple ketens, or oxomalonates, of somewhat similar structure. Thus, ethyl ketendicarboxylate, $CO:C(CO_2Et)_2$, is colourless, whereas diethylketen, $CO:CEt_2$, and ethyl oxomalonate, $CO(CO_2Et)_2$, are yellow. Furthermore, they are remarkably stable towards oxygen, even at higher temperatures, but in other respects they are highly reactive. They polymerise very readily to *cyclo*butanedione derivatives, but at widely different rates, and altogether they show how little can be predicted about the influence of a particular group on the reactivity of a compound.

In the cases of carbonyl compounds and ethylenes there are also perplexing irregularities in colour and tendency to polymerise. A table illustrating this feature is given.

Ethyl ethylketencarboxylate gradually decomposes at 200° into ethyl malonate and resins, and is completely polymerised after about forty minutes.

Methyl phenylketencarboxylate reacts with water to form methyl hydrogen phenylmalonate, m. p. 95°, and with aniline to yield *methyl phenylmalonanilate*, m. p. 109°, or with *p*-toluidine to form *methyl phenylmalon*-p-*toluidate*, m. p. 148—149°. It polymerises at 30° within about two days, giving methyl 1:3-diketo-2:4-diphenyl*cyclo*butane-2:4-dicarboxylate. This ester is readily depolymerised to the keten at 150°, whilst it reacts with water to form *methyl diphenylacetonedicarboxylate*, $CO(CHPh\cdot CO_2Me)_2$, m. p. 90—91°.

Ethyl ketendicarboxylate absorbs water from the air and deposits crystals of diethyl hydrogen methanetricarboxylate, which decompose in a few seconds into ethyl malonate and carbon dioxide. It reacts with alcohol to form ethyl methanetricarboxylate, and with aniline to form diethyl methanetricarbonanilide, whilst it changes gradually at 180° into ethyl methanetricarboxylate and a highly fluorescent resin. At 30° it is by no means completely polymerised, even after one hundred days, and at 100° it takes several days to effect polymerisation. The viscous, yellow polymeride, ethyl 1:3-diketo*cyclo*butanetetracarboxylate, is depolymerised at 150°, and reacts with water to form *ethyl acetonetetracarboxylate*, $CO[CH(CO_2Et)_2]_2$, which has b. p. 95—102°/0·3 mm., and behaves on titration as a weak, monobasic acid. J. C. W.

Relation between the Configuration and Rotation of Epimeric Monocarboxylic Sugar Acids. III. Phenylhydrazides. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, **31**, 623—626. Compare A., 1916, ii, 545).—Comparison of the rotations of the phenylhydrazides of the various sugar acids, including gluconic, mannonic, galactonic, allonic, and arabonic acids, indicates that the magnitude of the rotation of the α-carbon atom is not altogether constant even for the series of phenylhydrazides, but the rule of the relation of direction of the rotation to the configuration of the α-carbon atom remains valid. H. W. B.

Influence of Different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. Constitutional Formula of α-Amino-acids and of Betaine. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 88—96. Compare A., 1913, ii, 887; this vol., i, 195).—Glycine and alanine both retard the destructive action of sodium hydroxide on galactose, as they do on dextrose (*loc. cit.*). They also retard the inversion of sucrose by hydrochloric acid. Phenol also retards the action of the alkali on dextrose, but has no influence on the inversion of sucrose. Betaine does not influence the action of sodium hydroxide on dex-

trose, but retards the inversion of sucrose by acid. From these results the author draws the conclusion that glycine and alanine are best represented by the usual straight-chain formula when in alkaline or acid solution, and that betaine is best represented by the cyclic formula, $CO<\begin{smallmatrix}CH_2\\-O-\end{smallmatrix}>NMe_3$, in neutral and alkaline solutions and by the straight-chain formula, $CO_2H\cdot CH_2\cdot NMe_3Cl$, in acid solution. W. G.

Preparation of Lyxose. E. P. CLARK (*J. Biol. Chem.*, 1917, **31**, 605—607).—A detailed description of the preparation of lyxose on a large scale by the oxidation of calcium *d*-galactonate by means of hydrogen peroxide, using ferric acetate as a catalyst (compare Ruff and Ollendorff, A., 1900, i, 476). H. W. B.

Methylation by means of Formaldehyde. I. Mechanism of the Interaction of Formaldehyde and Ammonium Chloride. The Preparation of Methylamine and Dimethylamine. EMIL ALPHONSE WERNER (T., 1917, **111**, 844—853).—Brochet and Cambier have described the most favourable conditions for the production of methylamine hydrochloride by the interaction of formaldehyde and ammonium chloride (A., 1895, i, 325), and Knudsen (A., 1915, i, 220) has shown how dimethylamine and trimethylamine can be obtained as well in other circumstances. In discussing the mechanism of the reactions, it was assumed by these workers, in each case, that complex condensation products of formaldehyde and ammonia are the precursors of the methylamines, but it is now shown that a much simpler explanation is more probable.

The clue was found in an examination of the distillates obtained by heating mixtures of formalin (containing methyl alcohol, as usual) with ammonium chloride, methylamine hydrochloride, and dimethylamine hydrochloride. The noteworthy products in the first two cases were methyl formate and carbon dioxide, which shows that much formic acid is developed during the reaction. The series of changes is expressed by the following equations: (1) $H\cdot CHO + NH_3(HCl) = H_2O + CH_2{:}NH(HCl)$; (2) this $+ H_2O + H\cdot CHO = CH_3\cdot NH_2,HCl + H\cdot CO_2H$. The brackets, thus, $NH_3(HCl)$, are used to indicate highly dissociated salts. The formic acid is then partly esterified, but mainly oxidised to carbon dioxide and water.

(3) $CH_2O + CH_3\cdot NH_2(HCl) = H_2O + CH_2{:}NMe(HCl)$;
(4) this $+ H_2O + H\cdot CHO = NHMe_2,HCl + H\cdot CO_2H$; (5) $CH_2O + 2NHMe_2(HCl) = H_2O + CH_2(NMe_2)_2,2HCl$; (6) this $= NMe_3,HCl + CH_2{:}NMe(HCl)$; and, finally, in the absence of sufficient formaldehyde, the base, $CH_2{:}NMe$, would form the known trimeride (Brochet and Cambier). Naturally, reactions (2) to (4) overlap to a certain extent, but it is possible to separate the hydrochlorides of the bases easily by reason of the following facts: (*a*) ammonium chloride is practically insoluble in a concentrated solution of methylammonium chloride; (*b*) dimethylammonium chloride is

more soluble in water than methylammonium chloride, and the former is soluble in chloroform and the latter not. Trimethylamine (6) is only formed if the heating is prolonged or the temperature rises above 110°. Only polymerised condensation products like the base $(CH_2{:}NMe)_3$ give precipitates with picric acid, and no such precipitates can be obtained during the earlier stages of the reaction.

Details are given for the preparation of the methylamine and dimethylamine salts on a considerable and economical scale.

J. C. W.

Isomorphism of Nitrates and Chlorates. RENZO REA (*Gazzetta*, 1917, **47**, ii, 69—86).—The following compounds are completely isomorphous: $Ni(NO_3)_2,10H_2O,2C_6H_{12}N_4$; $Ni(ClO_3)_2,10H_2O,2C_6H_{12}N_4$; $Co(NO_3)_2,10H_2O,2C_6H_{12}N_4$; $Co(ClO_3)_2,10H_2O,2C_6H_{12}N_4$. The compound of magnesium chlorate and hexamethylenetetramine is isodimorphous with the compound of magnesium nitrate and hexamethylenetetramine. The corresponding cadmium salts are probably also isodimorphous.

The following crystallographic measurements are recorded: $Ni(NO_3)_2,10H_2O,2C_6H_{12}N_4$ is triclinic [$a:b:c=1{\cdot}0265:1:0{\cdot}9646$; $\alpha=60°36'$, $\beta=75°29'$, $\gamma=78°20'$]. $Ni(ClO_3)_2,10H_2O,2C_6H_{12}N_4$ is triclinic [$a:b:c=1{\cdot}0392:1:0{\cdot}9732$; $\alpha=60°55'$, $\beta=77°15'$, $\gamma=77°7'$].

$Co(NO_3)_2,10H_2O,2C_6H_{12}N_4$ is triclinic [$a:b:c=1{\cdot}0136:1:0{\cdot}9590$; $\alpha=60°30'$, $\beta=75°33'$, $\gamma=77°58'$]. $Co(ClO_3)_2,10H_2O,2C_6H_{12}N_4$ is triclinic [$a:b:c=1{\cdot}0192:1:0{\cdot}9636$; $\alpha=60°34'$, $\beta=75°38'$, $\gamma=78°1'$].

$Mg(NO_3)_2,10H_2O,2C_6H_{12}N_4$ is rhombic [$a:b:c=0{\cdot}8388:1:0{\cdot}4894$]. $Mg(ClO_3)_2,10H_2O,2C_6H_{12}N_4$ is triclinic [$a:b:c=1{\cdot}0240:1:0{\cdot}9692$; $\alpha=60°16'$, $\beta=76°33'$, $\gamma=77°11'$].

$Cd(NO_3)_2,5H_2O,C_6H_{12}N_4$ is monoclinic [$a:b:c=1{\cdot}1006:1:1{\cdot}1360$; $\beta=49°45'$]. $Cd(ClO_3)_2,5H_2O,C_6H_{12}N_4$ is monoclinic [$a:b:c=1{\cdot}0221:1:0{\cdot}9764$; $\beta=42°45'$]. R. V. S.

Chondrosamine and its Synthesis. P. A. LEVENE (*J. Biol. Chem.*, 1917, **31**, 609—621. Compare A., 1916, i, 712, 713).—The author brings forward conclusive evidence of the identity of natural chondrosamine and synthetic lyxohexosamine. All the derivatives prepared from chondrosamine have now been obtained from synthetic lyxohexosamine. The difference between the rotations of chondrosamine hydrochloride, $[\alpha]_D+129°$ (initial) and $+95°$ (equilibrium) (Levene and La Forge, A., 1914, i, 889) and of lyxohexosamine hydrochloride, $[\alpha]_D+53°$ (initial) and $+94{\cdot}2°$ (equilibrium) (Levene, *loc. cit.*), is shown to be due to the fact that the substance exists in two epimeric forms. The conditions for the isolation of either form have not been entirely elucidated, but natural chondrosamine has been obtained in both forms, one of which is identical with that in which the synthetic lyxohexosamine has so far always been obtained.

Lyxohexosaminic acid prepared from lyxosimine and hydrocyanic acid (Levene and La Forge, A., 1915, i, 944) is shown also to exist in two epimeric forms, which accounts for the variation in the rotations of different preparations of the synthetic acid. The lyxohexosamine obtained by reduction of lyxohexosamic acid yields, on oxidation with mercuric oxide by Pringsheim and Ruschmann's method (A., 1916, i, 506), a mixture of epimeric lyxohexosamic acids which is identical with the chondrosamic acid prepared from chondrosamine.

Both natural and synthetic hexosamines on oxidation with bromine yield the same *αα′*-anhydrotalonic acid, which, on further oxidation with nitric acid, produces an optically active anhydrotetrahydroxyadipic acid. When chondrosamic acid is deaminised, it yields anhydrogalactonic acid, which, on treatment with nitric acid, gives an optically inactive anhydrotetrahydroxyadipic acid. The synthetic lyxohexosamic acid yields the same products as the hexosamines. Since the synthetic acid is a mixture of two epimerides, one being chondrosamic acid, the inactive anhydrotetrahydroxyadipic acid must be anhydromucic acid, whilst the optically active acid must be anhydrotalomucic acid.

Chondrosamine and the synthetic lyxohexosamine also yield identical penta-acetates (compare Hudson and Dale, A., 1916, i, 597), both *α*- and *β*-forms being isolated. H. W. B.

Separation of Glutamic Acid from other Amino-acids. A. Corti (Brit. Pat., 106081, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 979).—The acid solution obtained after hydrolysis of albumins is filtered hot, and then sufficient alkali or alkaline-earth hydroxide or carbonate is added to neutralise both the free hydrochloric acid and that combined with the amino-acid, leaving the latter unaffected. When the liquid has cooled and remained for some days, the glutamic acid is separated by filtration or by centrifugal action, and purified from resinous matter by crystallisation from water and decolorised with charcoal. Other amino-acids can be obtained by treatment of the mother liquors.

H. W.

Synthesis of *β*-Ketonic Bases. C. Mannich (*Arch. Pharm.*, 1917, **255**, 261—276).—*β*-Ketonic bases are obtained by the reaction between acetone or diethyl ketone, 35% formaldehyde solution and ammonium salts, or, yet more readily, the hydrochloride of methyl- or dimethyl-amine. Thus by boiling a solution of 35% formaldehyde (1 mol.), dimethylamine hydrochloride (1 mol.), and acetone (5 mols.) for twelve hours, the hydrochloride, a very hygroscopic, crystalline salt, of *δ*-dimethylaminobutan-*β*-one, b. p. 50—52°/13 mm., is obtained; the *aurichloride* forms needles, m. p. 124—126°. By a similar reaction with methylamine hydrochloride several bases are formed which are difficult to separate, but *methyl-di-γ-ketobutylamine*, $NMe(CH_2{\cdot}CH_2{\cdot}COMe)_2$, has been isolated, which forms crystals, m. p. 132°, and yields a *picrate*, yellow

needles, *platinichloride*, orange-red prisms, and *aurichloride*, yellow prisms, m. p. 153° (decomp.).

The reaction between acetone, 35% formaldehyde, and ammonium chloride at the ordinary temperature for five weeks yielded a number of condensation products, but no individual constituent could be isolated.

When diethyl ketone is used in place of acetone, dimethylamine hydrochloride yields only *α-dimethylamino-β-methylpentan-γ-one*, $COEt\cdot CHMe\cdot CH_2\cdot NMe_2$, b. p. 59—61°/10 mm. (*hydrochloride*, m. p. about 105°; *aurichloride*, golden-yellow prisms, m. p. 71°), but methylamine hydrochloride yields five products, the quantities of which vary with the experimental conditions, (1) *β-methyl-Δ^{α}-penten-γ-one*, $CH_2:CMe\cdot COEt$, b. p. 117—119°/760 mm. (*semicarbazone*, leaflets, m. p. 158—159°); (2) *α-methylamino-β-methylpentan-γ-one*, $NHMe\cdot CH_2\cdot CHMe\cdot COEt$, b. p. 72—74°/13 mm. (*platinichloride*, orange-yellow crystals, m. p. 146—147°); (3) 1:3:5-*trimethyl*-4-*piperidone*, $NMe<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CO$, which is isolated as the *hydrochloride*, $C_8H_{15}ON,HCl$, prisms, m. p. about 235° (decomp.) (*platinichloride*, orange-yellow prisms, m. p. 204°; *hydrochloride* of the *oxime*, $C_8H_{16}ON_2,HCl$, m. p. 191—192°); (4) *αε-dimethylamino-βδ-dimethylpentan-γ-one*, $CO(CHMe\cdot CH_2\cdot NHMe)_2$, or *ββ-dimethylaminomethylpentan-γ-one*, $COEt\cdot CMe(CH_2\cdot NHMe)_2$, b. p. 112—113°/13 mm., which forms a slowly crystallising *hydrochloride*, *aurichloride*, golden-yellow rosettes, *picrate*, *platinichloride*, orange-yellow crystals, and the *hydrochloride* of the *oxime*, $C_9H_{21}ON_3,2HCl,H_2O$, large prisms, m. p. 188—190° (decomp.), and (5) *methyldi-γ-keto-β-methylamylamine*, $NMe(CH_2\cdot CHMe\cdot COEt)_2$, b. p. 147—150°/14 mm. (apparently with decomp.) (*hydrochloride*, very hygroscopic crystals, m. p. 104—106°; *methiodide*, crystals, m. p. 139°, and the *hydrochloride* of the *dioxime*,

$$C_{13}H_{27}O_2N_3,HCl,2H_2O,$$

crystals, m. p. 192° [decomp.]).

The reaction between 35% formaldehyde, ammonium chloride, and diethyl ketone at the b. p. yields several products, the only substance which could be isolated being 1:3:5-trimethyl-4-piperidone. C. S.

The Special Reactions in the Transformation of the Azides of the Carboxylic Acids. VII.—XIII. THEODOR CURTIUS (*J. pr. Chem.*, 1917, [ii], **95**, 168—256. Compare *ibid.*, 1916, **94**, 273).—[With BERNHARD VAN DER LAAN.]—VII. *Hydrazides and Azides of the Alkyl Ethers of Glycollic Acid.* —Ethyl ethoxyacetate, $OEt\cdot CH_2\cdot CO_2Et$, b. p. 52°/12 mm., n_D^{18} 1·404, was obtained by the action of ethyl diazoacetate on ethyl alcohol in the presence of a little sulphuric acid; it forms a *hydrazide*, $OEt\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, leaflets, m. p. 32° (*hydrochloride*, colourless crystals, m. p. 102—103° with decomp.; *benzylidene* compound, leaflets, m. p. 82°; *o-hydroxybenzylidene* derivative, needles, m. p. 99—100°), and with ethyl acetoacetate yields 3-methylpyrazolone; the former product, on treatment with sodium nitrite and

the calculated amount of hydrochloric acid, undergoes conversion into *ethoxyacetylazide*, $OEt\cdot CH_2\cdot CO\cdot N_3$, a heavy, pungent, pale yellow oil; this, when warmed with water, gives *ethoxymethylurethane*, $OEt\cdot CH_2\cdot NH\cdot CO_2Et$, a pleasant-smelling, viscid mass, which reacts with hydrochloric acid, producing a hygroscopic, crystalline mass, probably the *hydrochloride* of the urethane. With *p*-toluidine in ethereal solution the azide yields s-p-*tolylethoxymethylcarbamide*, $OEt\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot C_6H_4Me$, needles, m. p. 84° (decomp.).

Ethyl *n*-propoxyacetate, prepared similarly to the ethoxy analogue, was converted through the *hydrazide*,

$$OPr^{\alpha}\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

an uncrystallisable syrup (*benzylidene* derivative, lustrous, colourless leaflets, m. p. 65°; m-*nitrobenzylidene* derivative, needles, m. p. 118—119°), into n-*propoxyacetylazide*, $OPr^{\alpha}\cdot CH_2\cdot CO\cdot N_3$, a pungent, pale yellow oil, which reacts with alcohol at 55°, giving n-*propoxymethylurethane*, $OPr^{\alpha}\cdot CH_2\cdot NH\cdot CO_2Et$, a viscid, yellow mass (*hydrochloride*, colourless crystals).

Ethyl *iso*amyloxyacetate, obtained by the interaction of ethyl diazoacetate and amyl alcohol, gives a *hydrazide*,

$$C_5H_{11}\cdot O\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

a viscous, yellow liquid, n_D^{18} 1·468 (*hydrochloride*, hygroscopic powder; *picrate*, yellow needles, m. p. 113°; *benzylidene* derivative, m. p. 64°; p-*methylbenzylidene* derivative, yellow powder, m. p. 77·5°), and an *azide*, $C_5H_{11}\cdot O\cdot CH_2\cdot CO\cdot N_3$, a yellow, viscous oil of stupefying odour.

[With DAVID AUFHÄUSER.]—VIII. *Hydrazide and Azide of α- and β-Hydroxypropionic Acid.*—Ethyl lactate and hydrazine hydrate, when heated together for three to four hours, interact with formation of lactic hydrazide, $OH\cdot CHMe\cdot CO\cdot NH\cdot NH_2$ (*hydrochloride*, m. p. 149°; *benzylidene* compound, colourless crystals, m. p. 158°; *salicylidene* derivative, yellow crystals, m. p. 169°; *benzophenone* derivative, $C_{16}H_{16}O_2N_2$, colourless prisms or needles, m. p. 158—159°; *acetone* derivative, an unstable, uncrystallisable, yellow syrup; *ethyl acetoacetate* derivative, $C_9H_{16}O_4N_2$, pale yellow solid, decomp. near 200°). When kept for a long time, the viscous lactic hydrazide partly solidifies, giving a pasty mass containing the symmetrical *dilactic hydrazide*, $N_2H_2[CO\cdot CHMe\cdot OH]_2$, colourless, indistinct crystals, m. p. 151°. On careful treatment with sodium nitrite and hydrochloric acid, lactic hydrazide is converted into *lactic azide*, $OH\cdot CHMe\cdot CO\cdot N_3$, a pungent, yellow oil, which readily decomposes in moist air, giving acetaldehyde, ammonia, nitrogen, and carbon dioxide, and reacts with aniline, *p*-toluidine, and alcohol, yielding respectively lactanilide, lactotoluidide, and a mixture of acetaldehyde with ethyl allophanate.

Methyl β-hydroxypropionate, b. p. 177—184°/746 mm., D_4^{16} 1·105, obtained by the action of methyl iodide on the silver salt of the acid, is accompanied by a colourless liquid, b. p. 195—196°/746 mm., approximating to the composition $C_8H_{14}O_5$. The ethyl ester of β-hydroxypropionic acid reacts with hydrazine hydrate in alcoholic solution, giving a small quantity of a substance, silky scales,

decomp. near 240° without melting, which from its power of forming a *dibenzylidene* derivative, $C_{17}H_{18}ON_4$, m. p. near 240° (decomp.), is probably *β-hydrazinopropionic hydrazide*,

$$NH_2\cdot NH\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot NH_2.$$

The reaction mixture from ethyl β-hydroxypropionate and hydrazine hydrate in aqueous solution, on evaporation, yields a yellow residue which must contain *β-hydroxypropionohydrazide*, because this product forms a *benzylidene* derivative,

$$OH\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot N:CHPh,$$

m. p. near 200°, and also on treatment with sodium nitrite and hydrochloric acid in the presence of ether gives rise to traces of *β-hydroxypropionic azide.*

[With ALFRED GOLDBERG.]—IX. *Hydrazide and Azide of Diphenylglycollic Acid.—Diphenylglycollohydrazide*,

$$OH\cdot CPh_2\cdot CO\cdot NH\cdot NH_2,$$

needles, m. p. 168—169°, prepared by the action of hydrazine hydrate on an alcoholic solution of ethyl benzilate, forms a *hydrochloride*, m. p. 174—176° (decomp.), a *sodium* derivative, $C_{14}H_{13}O_2N_2Na$, m. p. near 158—160°, a *benzylidene* derivative, $C_{21}H_{18}O_2N_2$, needles, m. p. 198°, a *salicylidene* derivative, needles, m. p. 244—245°, an *acetone* derivative, $C_{17}H_{18}O_2N_2$, tablets, m. p. 190°, an *acetophenone* derivative, $C_{22}H_{20}O_2N_2$, needles, m. p. 180—181°, an *ethyl acetoacetate* derivative, $C_{20}H_{22}O_4N_2$, microscopic prisms, m. p. 114—115°, a *pyruvic* acid derivative, $C_{17}H_{16}O_4N_2$, needles, m. p. 197—198°, an *acetyl* derivative, $C_{16}H_{16}O_3N_2$, leafy crystals, m. p. 192—194°, and a *benzoyl* derivative, needles, m. p. 156—157°. In hot aqueous-alcoholic solution diphenylglycollohydrazide is converted by iodine into *bis-diphenylglycollohydrazide*, $N_2H_2[CO\cdot CPh_2\cdot OH]_2$, colourless needles, m. p. 256—257°. *Diphenylglycollic azide*, $OH\cdot CPh_2\cdot CO\cdot N_3$, obtained by the action of sodium nitrite on the aqueous solution of diphenylglycollohydrazide in the presence of acid, is an amorphous, resinous substance, which is decomposed by alcohol or water with formation of diphenylglycollamide and nitrogen; aqueous ammonia gives rise to a similar product, whilst in ethereal solution with *n*-propylamine, diethylamine, hydrazine hydrate, and phenylhydrazine respectively the analogous products are the n-*propylamide*, tablets, m. p. 80—82°, the *diethylamide*, needles, m. p. 95—96°, the hydrazide and the *phenylhydrazide*, needles, m. p. 139—141°, of diphenylglycollic acid; aniline and *p*-toluidine convert the azide into benzophenone, together with phenylcarbamide and *p*-tolylcarbamide respectively, whilst *m*-nitrobenzohydrazide yields benzophenone and m-*nitrobenzoylsemicarbazide*, needles, m. p. 202—203°.

[With CARL VON HOFE.]—X. *Hydrazide and Azide of Malic Acid.*—Ethyl malate reacts with hydrazine hydrate in alcoholic solution with formation of *malic hydrazide*,

$$NH_2\cdot NH\cdot CO\cdot CH_2\cdot CH(OH)\cdot CO\cdot NH\cdot NH_2,$$

an amorphous powder, m. p. 177·5° (*dihydrochloride*, needles, m. p. 189° (decomp.); *dibenzylidene* derivative, amorphous powder, m. p. 164°; *cinnamylidene* derivative, microcrystalline powder, m. p. 192°; *acetone* derivative, crystalline powder, m. p. 168°),

which by treatment with sodium nitrite solution in the presence of ether is convertible into *malic azide*, $N_3\cdot CO\cdot CH_2\cdot CH(OH)\cdot CO\cdot N_3$, a pale yellow oil of characteristic odour; this is decomposed by alcohol with production of a yellow, oily *urethane* compound, which is decomposed by cold dilute acids with liberation of carbon dioxide and formation of aminoacetaldehyde.

[With CHRISTIAN OHLGART.]—XI. *Hydrazide and Azide of Tartaric Acid.*—Tartarodihydrazide (compare Frankland and Slator, T., 1903, **83**, 1363), obtained from ethyl tartrate and hydrazine hydrate, forms a *dihydrochloride*, a *disalicylidene* derivative, $C_{18}H_{18}O_6N_4$ a yellowish-white powder, m. p. 261°, a colourless *di*-p-*anisylidene* derivative, m. p. 231°, a *dipiperonylidene* derivative, pale yellow leaflets, m. p. 216° (decomp.), a *dicinnamylidene* derivative, yellow powder, m. p. 218°, a colourless *di*-m-*nitrobenzylidene* derivative, m. p. 210°, an *ethyl acetoacetate* derivative, $C_{16}H_{28}O_8N_4$, colourless, crystalline powder, m. p. 151°, a *diacetyl* derivative, needles, m. p. 216°, and a *dibenzoyl* derivative, light grey crystals, m. p. 219° (decomp.). On treatment with iodine in aqueous alcoholic solution, the dihydrazide undergoes conversion into the cyclic *hydrazide*, $\begin{array}{l} NH\cdot CO\cdot CH\cdot OH \\ NH\cdot CO\cdot CH\cdot OH \end{array}$, a yellow powder, which begins to decompose near 220° without melting. The dihydrazide hydrochloride reacts with sodium nitrite solution, producing *tartaric diazide*,

$$N_3\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot N_3,$$

colourless crystals, m. p. 66° (decomp.), which is decomposed by aniline or toluidine at 100° with formation of tartaro-dianilide or -ditoluidide and by alcohol or water, giving glyoxal (m-*nitrobenzoylosazone*, $C_{16}H_{12}O_6N_6$, m. p. 320° with decomp.). The addition of phenylhydrazine acetate to a cold aqueous solution of the azide causes the deposition of tartarodiphenylhydrazide.

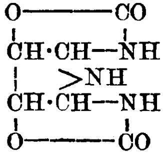
[With AUGUST DARAPSKY.]—XII. *Hydrazide and Azide of Mucic Acid.*—Ethyl mucate and hydrazine hydrate react in alcoholic solution, forming *mucodihydrazide*,

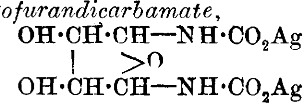
$$NH_2\cdot NH\cdot CO\cdot [CH\cdot OH]_4\cdot CO\cdot NH\cdot NH_2,$$

leaflets, m. p. 215° (decomp.) (*dihydrochloride*, m. p. 204° [decomp.]; *dibenzylidene* derivative, a colourless, amorphous mass, m. p. 221° (decomp.); *disalicylidene* derivative, m. p. 232° (decomp.); *acetone* derivative, $C_{12}H_{22}O_6N_4$, decomp. near 200°), which is converted by sodium nitrite into *mucic diazide*,

$$N_3\cdot CO[CH\cdot OH]_4\cdot CO\cdot N_3,$$

a microcrystalline powder; the action of aniline on this substance yields mucodianilide, whilst warm alcohol causes the production of free nitrogen, ethyl mucate, carbamic azide, tartardialdehyde, and *dihydroxytetrahydrofurandicarbamo-γ-dilactone* (annexed formula); the solution of the last-named substance in aqueous sodium hydroxide, on treatment with silver nitrate solution, yields the gelatinous *silver dihydroxytetrahydrofurandicarbamate*,





The action of methyl alcohol on mucic diazide is similar to that of ethyl alcohol, whilst water also yields the dilactone, together with tartardialdehyde.

[With FRIEDRICH SAUVIN.]—XIII. *Hydrazide and Azide of Citric Acid.*—Ethyl citrate and hydrazine hydrate in alcoholic solution react, giving *citrotrihydrazide*,

$$NH_2\cdot NH\cdot CO\cdot CH_2\cdot C(OH)(CO\cdot NH\cdot NH_2)\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

tablets, m. p. 107° (*trihydrochloride*, needles, m. p. 162°; *tribenzylidene* derivative, colourless crystals, m. p. 227°; *trisalicylidene* derivative, needles, m. p. 180° (decomp.); *benzophenone* derivative, $C_{45}H_{38}O_4N_6$, colourless needles, m. p. 159°), which by sodium nitrite is convertible into *citric triazide*,

$$N_3\cdot CO\cdot CH_2\cdot C(CO\cdot N_3)(OH)\cdot CH_2\cdot CO\cdot N_3,$$

colourless needles, which melt and then explode on warm water. In the presence of much water the triazide decomposes with formation of some azoimide, whilst aqueous ammonia causes the production of citramide, aniline, and *p*-toluidine in ethereal solution, analogously yielding citro-anilide and -*p*-toluidide respectively. Warm ethyl alcohol causes decomposition into free nitrogen and a red substance consisting probably of an impure urethane of the formula

$$CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot CH_2\cdot NH\cdot CO_2Et,$$

whilst dilute hydrochloric acid at 40° gives rise to diaminoacetone. By the interaction of ethyl citrate and hydrazine hydrate in the absence of alcohol there is obtainable *citrohydrazihydrazide hydrochloride*, $NH{<}{\substack{NH\cdot CO\\ CO\cdot CH_2}}{>}C(OH)\cdot CH_2\cdot CO\cdot NH\cdot NH_2,HCl$, decomp. near 200°, which reacts with benzaldehyde, giving the *benzylidene* derivative, $NH{<}{\substack{NH-CO\\ CO\cdot CH_2}}{>}C(OH)\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh$, a crystalline powder, m. p. near 274°, and with sodium nitrite yielding *citrohydraziazide*, $NH{<}{\substack{NH-CO\\ CO\cdot CH_2}}{>}C(OH)\cdot CH_2\cdot CO\cdot N_3$; this is a colourless powder which is converted by aniline in the presence of a little alcohol and ether into *citrohydrazianilide*,

$$NH{<}{\substack{NH-CO\\ CO\cdot CH_2}}{>}C(OH)\cdot CH_2\cdot CO\cdot NHPh,$$

m. p. near 267° (decomp.), and on heating with water gives a yellow, crystalline powder, decomp. near 280°, of uncertain nature.

D. F. T.

The Constitution of Carbamides. IV. The Mechanism of the Interaction of Carbamide [Urea] and Nitrous Acid. EMIL ALPHONSE WERNER (T., 1917, **111**, 863—876).—The reaction between nitrous acid and urea, usually expressed by the equation $CH_4ON_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O$, is commonly regarded as evidence of the carbamide structure, but, without asking why not, chemists have not used the reaction for the estimation of urea, knowing that it is quite valueless for the purpose. The author has now examined the reaction quantitatively, and proves that the above equation is fallacious, being based on a wrong conception of the constitution of urea and not on experimental evidence.

Urea is not attacked by pure nitrous acid, even if a small quantity of a weak acid (for example, acetic acid) is present. Only when a strong acid is present does a reaction take place, that is, the reaction is really that of a salt of urea. It can be demonstrated that one of the initial products is cyanic acid, which is hydrolysed as fast as it is formed, or attacked by more nitrous acid. The actual reactions can therefore be represented by the following equations:

$$(1)\ HN{:}C{<}{}^{NH_3}_{O} + HX = HN{:}C(OH){\cdot}NH_2,HX;$$

(2) this $+ HNO_2 = N_2 + HNCO + 2H_2O + HX$; (3) $HNCO + H_2O = NH_3 + CO_2$; (4) $HNCO + HNO_2 = CO_2 + N_2 + H_2O$. Reaction (4) can be almost entirely suppressed in favour of reaction (3) by keeping the concentration of nitrous acid low, and, conversely, if the solutions are concentrated and nitrous acid is in excess, reaction (4) is the predominating one, although it never quite outweighs reaction (3). Only if reaction (4) were quantitatively realised would the proportion of nitrogen to carbon dioxide in the gas conform to the usually accepted equation. The "loss" of nitrogen observed, regarded from the old point of view, is due to the production of ammonia (reaction 3). Another fact which has been overlooked is that nitric oxide is always formed as well, under the ordinary conditions used in the estimation of nitrous acid by urea, even to the extent of 6—8% of the total gas. J. C. W.

Electronic Formula of Benzene and Molecular Volumes of the Chlorobenzenes. HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1917, **39**, 1688—1699).—Various relationships between the electronic formula of benzene and certain physical properties, notably the molecular volumes, of mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes are indicated and discussed. It is shown that halogen atoms which function positively appear to possess different atomic volumes from those which function negatively, so that it is possible to correlate certain additive and constitutive effects apparent in the molecular volumes of certain compounds with their electronic formulæ; these effects cannot be explained by means of ordinary structural formulæ. Definite relationships which exist between the molecular volumes of six different chlorobenzenes and their respective electronic formulæ lend further support to the electronic formula of benzene. The suggestion is made that any variations in the relative positions of the valency electrons which determine the polarity of an atom may likewise cause variations in the atomic volume of the atom. T. H. P.

Preparation of Benzyl Chloride. J. B. CONANT (U.S. Pat., 1233986, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 1002).—A mixture of toluene and bleaching powder or other suitable chlorine compound is treated with sulphur dioxide or other suitable gas reacting with the bleaching powder to form chlorine, and the resulting benzyl chloride separated by distillation. H. W.

Reduction of Nitro- and Nitroso-compounds with Platinum and Hydrogen. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 87—91).—Aromatic mononitro-compounds (*p*-nitrophenol, *p*-nitroanisole, and *p*-nitrotoluene) are reduced to amines by hydrogen and platinum-black at the ordinary temperature, no matter what quantity of hydrogen is present. The aromatic nitroso-compounds behave in the same way (*p*-nitrosophenol, *p*-nitrosothymol, *p*-nitrosodimethylaniline, and the nitrosonaphthols). In the same conditions, terpene nitroso-compounds are reduced quantitatively to the corresponding hydroxylamines; thus, 8-nitrosomenthone is converted into 8-hydroxylaminomenthone. R. V. S.

Crystallographic Examination of Diphenyl and its Derivatives. KARL MIELEITNER (*Zeitsch. Kryst. Min.*, 1915, **55**, 51—87). —The author has examined crystals of about twenty-two ortho- and para-derivatives of diphenyl, but fails to find any certain evidence of morphotropic relationship between a derivative and the parent substance, and few instances of morphotropic relationship among the derivatives.

Diphenyl (m. p. 70°) is monoclinic prismatic [$a:b:c=1·4428:1:5·4331$; $\beta=94°46'$].

p-*p'*-Ditolyl is also monoclinic prismatic, but bears no apparent relationship to the parent hydrocarbon [$a:b:c=1·1780:1:0·7212$; $\beta=94°20'$].

p-*p'*-Difluoro-, dichloro-, and dibromo-diphenyl form an isomorphous monoclinic series; unfortunately, the di-iodo- and dicyano-compounds could not be completely measured. The axial ratios are as follows:

p-*p'*-Difluorodiphenyl [$a:b:c=1·1021:1:0·6954$; $\beta=96°8'$].
p-*p'*-Dichlorodiphenyl [$a:b:c=1·1504:1:0·7159$; $\beta=96°53'$].
p-*p'*-Dibromodiphenyl [$a:b:c=1·1152:1:0·6942$; $\beta=96°38'$].

Of the other derivatives of the dipara-series, the dihydroxydiphenyl is orthorhombic [$a:b:c=0·8555:1:4·0194$], whilst dinitrodiphenyl and diaminodiphenyl are triclinic.

The diortho-derivatives, although structurally less symmetrical, frequently crystallise with higher symmetry than the corresponding dipara-compounds. Thus, *o*-*o'*-dichlorodiphenyl is orthorhombic [$a:b:c=0·8297:1:0·7459$]; *o*-*o'*-dihydroxydiphenyl, orthorhombic [$a:b:c=1·1819:1:1·8277$]; *o*-*o'*-dinitrodiphenyl, monoclinic [$a:b:c=1·2927:1:0·9089$; $\beta=121°36\frac{1}{2}'$]; *o*-*o'*-diaminodiphenyl, monoclinic [$a:b:c=1·3522:1:3·3760$; $\beta=100°19\frac{1}{2}'$].

The crystals of other mono- and di-derivatives of diphenyl are described, and also those of di-diphenylmethane. It is concluded that the magnitude of the change of crystal structure effected by any substituent group bears no relation to the size of that group. The topic parameters appear to throw no fresh light on the morphotropic relationships. E. H. R.

Pyro-condensations in the Aromatic Series. II. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1917, **38**, 141—157. Compare *ibid.*, 1917, **37**, 681).—Aromatic derivatives of the four

halogens have been maintained for some hours at a bright red heat and the products examined. In all cases, halogen and hydrogen are eliminated together; it is never found, except perhaps to a doubtful extent in the case of iodine, that two aromatic nuclei are united by the carbon atoms which bore the halogen atoms.

Chlorobenzene yields 4:4′-dichlorodiphenyl and some *p*-chlorodiphenyl and 2:2′-dichlorodiphenyl, hydrogen chloride and a trace of chlorine being evolved. *p*-Dichlorobenzene is particularly stable, but gives after a time 2:5:2′:5′-*tetrachlorodiphenyl*, yellow crystals, m. p. 84—85°.

The decomposition of bromobenzene is greatly helped by mercury vapour. The products are benzene and *p*-bromodiphenyl, m. p. 87—88°. *p*-Dibromobenzene yields 4:4′-dibromodiphenyl, m. p. 162—163°; 2:4′- or 2:2′-dibromodiphenyl, m. p. 117°, a very little bromobenzene, and sometimes 2:5:2′:5′-tetrabromodiphenyl, m. p. 210—211°.

Iodobenzene yields benzene, some diphenyl, and a mixture of iododiphenyls.

Fluorobenzene forms 4:4′-difluorodiphenyl, m. p. 94—95°.

o-Bromotoluene most readily yields anthracene and probably 2:2′-dibromostilbene and 2:2′-dibromodiphenyl. *p*-Chlorotoluene gives 4:4′-dichlorodibenzyl and 4:4′-dichlorostilbene. *p*-Fluorotoluene decomposes quickly and at not a very high temperature, but the only important product is 4:4′-*difluorostilbene*, $C_{14}H_{10}F_2$, m. p. 106°. This slowly combines with bromine to form 4:4′-*difluoro-αα′-dibromodibenzyl*, in compact needles, m. p. 141—142°. *m*-Fluorotoluene yields chiefly 3:3′-*difluorodibenzyl*, which crystallises in broad lamellæ, m. p. 38°. *p*-Iodotoluene forms some toluene, dibenzyl, stilbene, and 4:4′-*di-iodostilbene*, colourless leaflets, m. p. 257—259°.

Benzyl chloride yields stilbene, toluene, and a trace of dibenzyl, but no phenanthrene. J. C. W.

Tetraphenylmethane. M. GOMBERG and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1917, **39**, 2009—2015).—A report of attempts to improve the yield of tetraphenylmethane obtainable by various methods. The action of magnesium phenyl bromide on chlorotriphenylmethane gives only a poor yield of tetraphenylmethane, the product being largely triphenylmethyl; this result is not due to the subsequent decomposition of tetraphenylmethane by the Grignard reagent or to a primary formation of triphenylmethyl followed by a slow reaction of this with the Grignard reagent producing tetraphenylmethane. It is found, however, that when the action is effected in the absence of ether and at 150—200°, 10—12% of the tetraphenyl compound can be obtained instead of the usual 3—5%, and the product is not contaminated with triphenylmethyl peroxide as is the ordinary product at lower temperatures.

The methyl and ethyl ethers of triphenylcarbinol react with magnesium phenyl bromide at 150—160°, giving 10—12% of tetraphenylmethane, whilst with the phenyl ether the yield is 20%.

Triphenylcarbinol and chlorotriphenylmethane readily condense with phenol at 100° in the presence of a small quantity of an acid, such as sulphuric or hydrochloric, forming *p*-hydroxytetraphenylmethane in almost quantitative amount; if sodium phenoxide is used and the presence of acid is avoided, the product is phenoxytriphenylmethane, the occasional simultaneous presence of hydroxytetraphenylmethane in the product being probably due to an intermediate formation of triphenylmethyl, which subsequently reacts additively with the free phenol present. From the readiness with which *p*-hydroxytetraphenylmethane is produced, it is evident that the hindrance to the formation of tetraphenylmethane is not of a simple steric nature. D. F. T.

Amides and Imides of Tartaric Acid. III. L. CASALE (*Gazzetta*, 1917, **47**, ii, 63—68. Compare this vol., i, 545).—When *p*-phenetidine hydrogen tartrate is kept at 150—155° for some hours, p-*ethoxyphenyltartrimide*,

$$\begin{array}{l} CH(OH)\cdot CO \\ | \\ CH(OH)\cdot CO \end{array}\!\!>N\cdot C_6H_4\cdot OEt,$$

is formed (yield, 65%). The imide is insoluble in cold water and is not saponified when boiled with water for a long time; it has m. p. 260° (corr.), $[\alpha]_D^{14}$ +115·7°. When this imide is heated at 150—160° with an equal weight of *p*-phenetidine, *diethoxyphenyltartramide*, $C_{20}H_{24}O_6N_2$, m. p. 282° (corr.), is formed. *Ethoxyphenyltartramide*, $C_{12}H_{16}O_5N_2$, is produced when the above-mentioned imide is dissolved in warm concentrated aqueous ammonia; it crystallises in colourless, prismatic tablets, m. p. 237° (corr.; decomp.). *Ethoxyphenyltartramic acid*, $C_{12}H_{15}O_6N$, is obtained by boiling the imide with a 2*N*-solution of potassium hydroxide and acidifying the solution with concentrated hydrochloric acid. It crystallises in leaflets, m. p. 201° (corr.), and has $[\alpha]_D^{14}$ +107·1°. Its *methyl* ester, $C_{13}H_{17}O_6N$, forms shining prisms, m. p. 191° (corr.), $[\alpha]_D^{15}$ +101·2°. The *ethyl* ester, $C_{14}H_{19}O_6N$, crystallises in colourless prisms, m. p. 175° (corr.), and has $[\alpha]_D^{14}$ +98·72°.

R. V. S.

Steric Hindrance of Chemical Reactions. III. ψ-Cumylsulphamic Acid [ψ-Cumylaminosulphonic Acid]. C. PAAL and MAX HUBALECK (*Ber.*, 1917, **50**, 1110—1115. Compare A., 1899, i, 587, 748; 1901, i, 693).—ψ-Cumidine reacts with aminosulphonic acid at moderate temperatures to form *ψ-cumidine aminosulphonate*, $NH_2\cdot SO_3H,NH_2\cdot C_6H_2Me_3$, in stout, elongated, glistening leaflets, m. p. 163°, which changes at 165—170° into *ammonium ψ-cumylaminosulphonate*, $C_6H_2Me_3\cdot NH\cdot SO_3\cdot NH_4$. When a mixture of ψ-cumidine and aminosulphonic acid is heated at 170—180°, however, the product is *ψ-cumidine ψ-cumylaminosulphonate*, which crystallises in concentric groups of sparingly soluble, glistening needles, m. p. 213°. This can be converted into the corresponding *barium* and *sodium* ($1H_2O$) salts, and from the latter the free *ψ-cumylaminosulphonic acid* (2:4:5-*trimethyl-*

phenylaminosulphonic acid) can be isolated in satiny needles, decomp. 225°.

It was found to be impossible to obtain either of the two possible ψ-cumidinesulphonic acids, by heating these ψ-cumylaminosulphonates, or by the action of fuming sulphuric acid on ψ-cumidine. J. C. W.

ψ-Cumylnitrosoaminosulphonic Acid. C. PAAL and MAX HUBALECK (*Ber.*, 1917, **50**, 1115—1118).—A suspension of ψ-cumylaminosulphonic acid in water, when treated with sodium nitrite in the cold, gives a crystalline mass of the sodium salt of the nitroso-acid, from which the free acid can be isolated by the careful addition of dilute hydrochloric acid at a low temperature. *ψ-Cumylnitrosoaminosulphonic acid* (2 : 4 : 5-*trimethylphenylnitrosoaminosulphonic acid*), $C_6H_2Me_3 \cdot N(NO) \cdot SO_3H$, crystallises in white needles, and greatly resembles diazonium salts. It explodes on warming, and even spontaneously when dry, and may also explode when warmed with dilute acids. With slightly acidified water, it decomposes into nitrogen and ψ-cumenol, and when warmed with alcohol it yields ψ-cumene. J. C. W.

The Three Nitrotriphenylamines. JEAN PICCARD and LOUIS M. LARSEN (*J. Amer. Chem. Soc.*, 1917, **39**, 2006—2009).—By heating with iodobenzene, potassium carbonate, copper powder, and a little potassium iodide, a nitrobenzene solution of *p*-nitrodiphenylamine was made to yield the corresponding *p*-nitrotriphenylamine, m. p. 140°, identical with the product obtainable by direct nitration of triphenylamine (Herz, A., 1890, 1409). In a similar manner, *o*- and *m*-nitrodiphenylamines respectively were converted into the previously unknown o-*nitrotriphenylamine*, $C_{18}H_{14}O_2N_2$, orange-yellow crystals, m. p. 98°, and m-*nitrotriphenylamine*, a lemon-yellow solid, m. p. 78°, the solution of which in sulphuric acid acquires a blue coloration in a few seconds.
D. F. T.

The Bromination of the Two Naphthylamines. HARTWIG FRANZEN and ERLING AASLUND (*J. pr. Chem.*, 1917, [ii], **95**, 160—167. Compare Franzen and Eidis, A., 1914, i, 162; Franzen and Henglein, A., 1915, i, 230).—It has already been shown that the naphthylamines, by conversion into their benzylidene derivatives, addition of bromine, and subsequent decomposition of the additive compounds, can be made to yield bromo-substituted naphthylamines. Further experiments are now described, as a result of which it is possible to state that only two atoms of bromine can with ease be introduced into α-naphthylamine, whilst the introduction of three is possible with β-naphthylamine.

1 : 2-Dibromo-β-naphthylamine, which has already been prepared in the above way, forms a *benzylidene* derivative, $C_{12}H_{11}NBr_2$, yellow needles, m. p. 101—103°; the dark grey dibromide, $C_{12}H_{11}NBr_4$, of this substance when boiled with alcohol regenerates the dibromonaphthylamine.

1-Bromobenzylidene-β-naphthylamine when successively treated in chloroform solution with bromine, pyridine, bromine, and boiling alcohol is converted into 1 : 6 : ?-tribromo-β-naphthylamine (compare Claus and Philipson, A., 1891, 462), which, like 2 : 4 : 6-tribromoaniline, does not form a benzylidene derivative. In an attempt to prepare a tetrabromo-derivative of β-naphthylamine, benzylidenenaphthylamine was thrice treated with bromine and pyridine successively, and then finally with bromine and alcohol successively, but the product was only the 1 : 6 : ?-tribromo-β-naphthylamine.

Benzylidene-α-naphthylamine is, by this method, readily convertible into 2 : 4-dibromo-α-naphthylamine, which, however, resisted the endeavour at further bromination by this process, the product obtained by decomposition of the dibromide of the benzylidene derivative being impure 2 : 4-dibromo-α-naphthylamine, the same substance being formed from benzylidene-α-naphthylamine after two successive treatments with bromine and pyridine and a final treatment with bromine and alcohol. D. F. T.

Preparation of Phenyl-α-naphthylamine. M. Katayama (*Kogyo-Kwagaku-Zasshi*; [*J. Chem. Ind., Tokyo*], 1917, **20**, 353—365; from *J. Soc. Chem. Ind.*, 1917, **36**, 865).—Streiff's method of preparing phenyl-α-naphthylamine by combination of α-naphthylamine hydrochloride and aniline is tedious and gives a relatively poor yield. The author made experiments to ascertain the most suitable conditions for preparing the base by Friedländer's method of condensing aniline with α-naphthol in presence of a dehydrating agent. Under the following conditions, a yield of 64% of the theoretical quantity of phenyl-α-naphthylamine (calculated on the α-naphthol used) is obtained. An intimate mixture of α-naphthol (1 mol.), aniline (2 mols.), and calcium chloride (1 mol.) is placed in an autoclave, which is heated for ten hours at 300°. The product is treated with boiling water to remove calcium chloride, with hydrochloric acid to remove uncombined aniline, and with sodium hydroxide to remove uncombined α-naphthol, and is then distilled in a vacuum in a current of carbon dioxide or hydrogen. After crystallising from alcohol, the phenyl-α-naphthylamine has m. p. 60°. T. S. P.

The Influence of the Solvent on the Reaction between Polyhydric Phenols and Alkali Hydrogen Carbonates. Franz von Hemmelmayr (*Monatsh.*, 1917, **38**, 77—89. Compare A., 1913, i, 468; 1915, i, 543).—The reaction between potassium hydrogen carbonate and polyhydric phenols under different conditions has been studied.

A. *Anhydrous Agents; Atmospheric Pressure.*—Resorcinol, at 120°, yields 2 : 4- and 2 : 6-dihydroxybenzoic acids; catechol and quinol produce no carboxylic acids. Pyrogallol yields 2 : 3 : 4-trihydroxybenzoic acid.

B. *Anhydrous Agents; Closed Tubes.*—Catechol at 200° yields catecholdicarboxylic acid; resorcinol forms α-resodicarboxylic acid, and 3 : 5-dihydroxybenzoic acid yields β-resodicarboxylic acid; quinol

at 260—270° gives a high yield of a dicarboxylic acid, which crystallises in needles with $1H_2O$; pyrogallol at 200° forms gallocarboxylic acid, m. p. 281°, the yield being almost the theoretical one; orcinol gives *p*-orsellinic acid. 1:5-Dihydroxynaphthalene at 230° yields a *dicarboxylic acid*, which decomposes at 290° and then melts at 300°; the acid and its alkali salts dye wool yellow, and the shade is converted into a very good brown by treatment with chromic acid or chromates. The *barium*, *calcium*, *silver*, and *ammonium* salts are described. 1:6-Dihydroxynaphthalene reacts with a mixture of the hydrogen carbonate and normal carbonate to form a *monocarboxylic acid*, in stellate groups of yellow prisms, m. p. 200°; the *barium* salt crystallises with $8H_2O$. Other dihydroxynaphthalenes were examined, but no acids could be obtained.

C. *Reactions in the Presence of Dry Aniline or Diphenylamine; Atmospheric Pressure.*—Resorcinol yields β-resorcylic acid and also α-resodicarboxylic acid, especially with diphenylamine, although this acid loses carbon dioxide most readily if heated alone with the bases. Catechol and quinol do not react, and pyrogallol forms only a monocarboxylic acid.

D. *Reactions in Boiling Anhydrous Cetyl Alcohol.*—Although this alcohol boils at a higher temperature than diphenylamine, the yield of α-resodicarboxylic acid from resorcinol is not so great as in the above case. J. C. W.

Compounds of Ferric Chloride with Ethyl Ether and with Benzyl Sulphide. AQUILA FORSTER, CHRISTOPHER COOPER, and GEORGE YARROW (T., 1917, **111**, 809—814).—Anhydrous ferric chloride dissolves in ethyl ether to form the dark red, very deliquescent *compound*, $C_4H_{10}O,FeCl_3$. This gives a quantitative yield of ethyl chloride when heated over a free flame, and reacts with ammonia to form products which evolve ethylamines on distillation.

A double *compound* of benzyl sulphide and ferric chloride, $S(C_7H_7)_2,FeCl_3$, has also been obtained, in minute, lemon-yellow crystals, m. p. 94°. This reacts with benzyl chloride to form tribenzylsulphinium ferrichloride, m. p. 98·5° (Hofmann and Ott, A., 1907, i, 84), which can be converted into the impure, viscous chloride by means of alkali. A *compound*, $S(C_7H_7)_3{\cdot}CN,FeCl_3$, lemon-yellow crystals, m. p. 76°, is obtained by the interaction of benzyl sulphide, benzyl cyanide, and ferric chloride in ethereal solution. Ammonia converts this into *tribenzylsulphinium cyanide*, $S(C_7H_7)_3{\cdot}CN$, large, white prisms, m. p. 41°, which combines with platinum chloride, as well as with ferric chloride, giving a red *compound*, $C_{44}H_{42}N_2S_2,PtCl_4$, m. p. 162°. J. C. W.

***p*-Dimethylaminobenzoyl Chloride.** H. STAUDINGER and R. ENDLE (*Ber.*, 1917, **50**, 1046—1047).—p-*Dimethylaminobenzoyl chloride* may be obtained in white leaflets, m. p. 145—147°, by the action of thionyl chloride on the corresponding acid, and converted into p-*dimethylaminobenzanilide*, m. p. 182—183°. Just as the reactivity of the carbonyl group in benzaldehyde or benzophenone

is greatly enhanced by the presence of a methoxyl or dimethylamino-group in the para-position, so *p*-methoxy- and especially *p*-dimethylamino-benzoyl chlorides are found to be more chemically active than benzoyl chloride. J. C. W.

Action of Sodium Benzyl Cyanide with Ethyl *p*-Tolylcinnamate. MILO REASON DAUGHTERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1927—1930).—The interaction of ethyl *p*-tolylcinnamate, benzyl cyanide, and sodium methoxide did not follow the expected course. but yielded *γ-cyano-γ-phenyl-β-*p*-tolylbutyric acid*,

$$CN\cdot CHPh\cdot CH(C_6H_4Me)\cdot CH_2\cdot CO_2H,$$

m. p. 166—169°, together with a substance which, from analogy with the results of Avery and McDole (A., 1908, i, 343), may have the constitution $CN\cdot CPh{<}{\begin{matrix}CH(C_6H_4Me)\cdot CH_2\cdot CO\\CH(C_6H_4Me)\cdot CH_2\cdot CO\end{matrix}}{>}O.$ D. F. T.

Method of Separation of Stereoisomeric α-Halogenated Ethylenic Acids (Stable and Labile). J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], **21**, 172—174).—The method used for the separation of the stereoisomeric α-iodocinnamic acids (compare A., 1916, i, 817) is shown to be generally applicable to α-halogenated ethylenic acids, and more detailed instructions are given. W. G.

β-Alkylated Cinnamic Acids and their Stereoisomerides. R. STOERMER, F. GRIMM, and E. LAAGE (*Ber.*, 1917, **50**, 959—980). —A number of β-alkylcinnamic acids and their esters, amides, and anilides are described, of both stable and *allo*-forms. Each pair of acids is remarkable among stereoisomeric acids in giving solid solutions of the two forms, which often appear to be composed of one kind of crystal, and are extremely difficult to separate. Furthermore, it frequently happens that the *allo*-acid has a higher m. p. than the stable acid, although the usual rule is observed in all but the case of the β-ethylcinnamic acids, namely, that the isomeride with the lower m. p. has by far the greater solubility. Consequently, it is often difficult to determine in those cases in which both forms are produced during the same synthesis which is the stable and which the *allo*-modification. The amides and anilides show similarly irregular physical properties, but the methyl esters regularly have lower boiling points in the *allo*-series and the *allo*-acids can be converted into indones (this vol., i, 654). The acids may usually be separated by means of light petroleum, but, owing to the prevailing scarcity of this solvent, other methods have been investigated. It is found that the basic copper salts of the *allo*-ethyl- and -propyl acids are much less soluble in ether than the isomerides, but the acids are all so weak that they do not yield aniline salts, and a separation by means of these is therefore impossible. The mixtures of isomerides are all much more soluble than either ingredient.

The labile acids may all be prepared by exposing the stable acids to the light of a quartz mercury lamp, and the methyl esters are obtained by means of methyl sulphate, in order to avoid any agents which favour transformation of the *allo*-form.

Stable β-methylcinnamic acid is best obtained by the action of

zinc filings and ethyl bromoacetate on acetophenone, a few drops of phosphoryl chloride being added before the distillation to ensure the complete decomposition of the β-hydroxy-acid which is first formed. The acid crystallises in rhombic prisms, m. p. 98·5°, and dissolves in sulphuric acid with lemon-yellow colour; the methyl ester forms large, stout crystals, m. p. 29°, b. p. 127—128°/10 mm.; the *amide* crystallises in stout needles, m. p. 119°; the anilide forms slender needles, m. p. 121° (compare Henrich and Wirth, A., 1904, i, 431). allo-β-*Methylcinnamic acid* crystallises in very thin, flat rhombs, m. p. 131·5°; the *methyl* ester has m. p. 26·5—27·5°, b. p. 113·5°/8 mm.; the *amide* forms iridescent leaflets, m. p. 94—95°; the *anilide* separates as a woolly mass, m. p. 93°.

β-Ethylcinnamic acid, obtained in a similar manner from propiophenone, crystallises in very large, elongated platelets, m. p. 95·5°; the *methyl* ester has b. p. 130°/8 mm.; the *amide* forms asbestos-like needles, m. p. 104°; the *anilide* has m. p. 84°. allo-β-*Ethylcinnamic acid* crystallises in stout rhombs, m. p. 93—95·5°; the *methyl* ester has b. p. 122—123°/8 mm.; the *amide* forms iridescent leaflets, m. p. 101°; the *anilide* has m. p. 122°.

β-Propylcinnamic acid, likewise obtained by Schroeter's method (A., 1907, i, 530), has m. p. 94°, and the *amide* forms woolly needles, m. p. 98·5°. allo-β-n-*Propylcinnamic acid* crystallises in long, stout needles, m. p. 86·5°, and the *amide* forms glistening leaflets, m. p. 100—101°. A mixture of the two acids forms homogeneous crystals, m. p. 59—60°.

p-β-Dimethylcinnamic acid (*ibid.*) crystallises in stout fibres, m. p. 135°; the methyl ester forms thin leaflets, m. p. 45—45·5°, b. p. 157°/17 mm.; the *amide* has m. p. 131—132°. allo-p-β-*Dimethylcinnamic acid* crystallises in brilliant leaflets, m. p. 117·5—118°; its *methyl* ester has b. p. 144—145°/17 mm.; the *amide* forms long needles, m. p. 106°.

o-*Methoxy-β-methylcinnamic acid* may be prepared from *o*-methoxyacetophenone and methyl bromoacetate, whereby precautions are necessary to avoid obtaining a mixture with the *allo*-modification. The stable acid forms feathery tablets, m. p. 96·5°, and the *methyl* ester has b. p. 172—173°/26 mm. allo-o-*Methoxy-β-methylcinnamic acid* may be obtained by the action of ultra-violet light on the stable acid or by hydrolysing 4-methylcoumarin (A., 1908, i, 339) and methylating the phenolic acid, thus:

$$C_6H_4{<}\begin{matrix}O\text{—}CO\\ CMe{:}CH\end{matrix} \longrightarrow OMe{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}CO_2H.$$

It has m. p. 123—124°, and its *methyl* ester has b. p. 157·5—158·5°/25 mm.

p-Methylcinnamic acid crystallises in large scales, m. p. 198—199°; its methyl ester has m. p. 57—58°, b. p. 164—165°/32 mm.; its *amide* forms white leaflets, m. p. 189—190°. allo-p-*Methylcinnamic acid* crystallises in bundles of stout needles, m. p. 75—76°, and forms an *aniline hydrogen* salt, woolly needles, m. p. 86—87°, a *methyl* ester, b. p. 141—142°/23 mm., and an *amide*, m. p. 116—116·5°. J. C. W.

The Optical Isomerism of the Abietic Acids. FERD. SCHULZ (*Chem. Zeit.*, 1917, **41**, 666—667).—Abietic acid may be prepared by extracting American colophony with dilute alcohol or by precipitating the alcoholic solution with hydrogen chloride, but the author finds that whereas the alcoholic solution of the resin has +rotation, the solution becomes lævorotatory on addition of hydrogen chloride, so that the products above mentioned are probably not identical. When the resin is dissolved in boiling alcohol and dry hydrogen chloride passed into the cold solution, white crystals of abietic acid are obtained, the constants of which gradually alter on recrystallisation from acetone, from $[\alpha]_D$ $-77{\cdot}9°$ (solvent and concentration not stated) and m. p. 161° to $[\alpha]_D$ $-96{\cdot}8°$, m. p. 171°. Further recrystallisation from acetone raises the m. p. to 173°. The molecular weight by titration is found to be 304. On exposure to air, the rotation alters owing to oxidation, and it changes also on heating at high temperatures (200°). American colophony, type H, extracted with dilute alcohol, yields an oil which gradually sets to a mass of crystals, from which by crystallisation from acetone a portion is obtained having $[\alpha]_D$ $-22°$ ($c=2{\cdot}2$; solvent not stated), whilst another part has $[\alpha]_D$ $+49°$. An almost inactive fraction, $[\alpha]_D$ $+2{\cdot}6°$, is also obtained. On treatment with mineral acid, the rotation of the two last became negative.

From technical resin oil the author has extracted an acid which he names *oilsylvic acid* (Ölsylvinsäure), m. p. 171—173°, $[\alpha]_D$ $+53°$ ($c=10$; solvent not stated), which does not alter in rotation when warmed with mineral acids, and in contradistinction to the abietic acid from colophony does not absorb oxygen from the air and does not turn yellow in light. The abietic acids can readily be esterified by boiling their alcoholic solutions with 30% of concentrated sulphuric acid for an hour. T. S. PA.

Iron Compounds of Salicylic Acid. R. F. WEINLAND and KURT ZIMMERMANN (*Arch. Pharm.*, 1917, **255**, 204—232).—The paper is largely a reply to Claasz's criticisms (*Arch. Pharm.*, 1915, **253**, 342) of Weinland and Herz's classification of the ferric compounds of salicylic acid into three groups (A., 1913, i, 1189). The substance to which Claasz gives the formula

$$OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}Fe{<}{}^{O\text{———}}_{O\cdot CO}{>}C_6H_4$$

is shown to contain varying amounts of bivalent iron and to be a mixture of salicylic acid compounds of bi- and ter-valent iron. The same is also true of Claasz's compound,

$$C_6H_4{<}{}^{O\text{———}}_{CO\cdot O}{>}Fe{\cdot}O{\cdot}Fe{<}{}^{O\text{———}}_{O\cdot CO}{>}C_6H_4.$$

Weinland and Herz's hexasalicylatotriferric salicylate (*loc. cit.*) cannot have the constitution given to it by Claasz. By treating an alcoholic solution of the substance with *N*-nitric acid, 20% perchloric acid solution, and concentrated sulphuric acid respectively, salts of the following composition have been obtained:

$$\text{(i)}\ \left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ OH\end{matrix}\right]\begin{matrix}NO_3\\ CO_2\cdot C_6H_4\cdot OH\end{matrix}+\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ OH\end{matrix}\right](O\cdot CO\cdot C_6H_4\cdot OH)_2+15\text{ or }4H_2O,$$

brownish-red rectangular plates, (ii) $\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ (OH)_2\end{matrix}\right]ClO_4+\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ (OH)_2\end{matrix}\right]O\cdot CO\cdot C_6H_4\cdot OH+4H_2O,$
brownish-yellow, crystalline powder, and

$$\text{(iii)}\ \left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ (OH)_2\end{matrix}\right](O\cdot CO\cdot C_6H_4\cdot OH)+\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\ (OH)_2\end{matrix}\right]_2SO_4+\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_5\\ (OH)_8\end{matrix}\right](O\cdot CO\cdot C_6H_4\cdot OH)+8H_2O,$$

yellowish-red, crystalline powder. C. S.

Metallic Salts of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. M. Bouvet (*Bull. Sci. Pharmacol.*, 1917, **24**, 86—90; from *Chem. Zentr.*, 1917, ii, 101—102).—The author describes the preparation of aspirin and its known mineral salts. *Magnesium* o-*acetoxybenzoate* is obtained by treating aspirin with calcined magnesia and water; the precipitate is extracted with methyl alcohol, and the solution precipitated with ether. The salt crystallises in hexagonal plates with 3 or $4H_2O$, which are soluble in water or methyl alcohol, but slightly so in ethyl alcohol. A bibliography of other salts is given. H. W.

Ketens. XXVIII. Ketencarboxylic Esters and Schiff's Bases. H. Staudinger (*Ber.*, 1917, **50**, 1035—1041).—The author has previously found that coloured ketoketens react with Schiff's bases, but he believed that colourless ketens were less reactive. He now reports that no such connexion between colour and additive capacity exists.

[With R. Endle.]—Benzylideneaniline reacts with ordinary keten at 180—200° to form the *lactam* of *β-anilino-β-phenylpropionic acid*, $NPh<\begin{matrix}CHPh\\ CO\end{matrix}>CH_2$, which crystallises in long leaflets, m. p. 153—154°, and decomposes at 600° into phenylcarbimide and styrene.

[With J. Modrzejewski.]—Ethyl ketencarboxylate and benzylideneaniline unite at −20° to form *ethyl* 3-*keto*-1 : 2-*diphenyl*-4-*ethyltrimethylenimine*-4-*carboxylate* (I), m. p. about 66°. This is very unstable, and changes at 200° into the *lactam* of *α-carbethoxy-β-anilino-β-phenyl-α-ethylpropionic acid* (II), m. p. 109—110°, which may be hydrolysed to the free *acid* (III), m. p. 154—155°.

$$\underset{\text{(I.)}}{CO_2Et\cdot CEt<\begin{matrix}CO\\ NPh\end{matrix}>CHPh}\longrightarrow\underset{\text{(II.)}}{CO_2Et\cdot CEt<\begin{matrix}CO\\ CHPh\end{matrix}>NPh}\longrightarrow$$

$$\underset{\text{(III.)}}{NHPh\cdot CHPh\cdot CHEt\cdot CO_2H.}$$

[With H. HIRZEL.]—Methyl phenylketencarboxylate reacts with benzylideneaniline to yield the *lactam* of *α-carbomethoxy-β-anilino-αβ-diphenylpropionic acid*, $CO_2Me\cdot CPh<\begin{matrix}CO\text{---}\\ CHPh\end{matrix}>NPh$, m. p. 158—159°, and with diphenylmethyleneaniline (benzophenoneanil) to form *methyl* 4 : 6-*diketo*-1 : 2 : 2 : 3 : 5-*pentaphenylpiperidine*-3 : 5-*dicarboxylate*, m. p. 213—214° (decomp.).

Ethyl ketendicarboxylate does not react with benzylideneaniline, but with benzophenoneanil it forms a trimethyleneimine derivative.

J. C. W.

Certain Derivatives of *p*-Dialkylamino-*o*-benzoylbenzoic Acids. J. PÉRARD (*Ann. Chim.*, 1917, [ix], **7**, 340—414; **8**, 22—69).—In part a more detailed account of work already published (compare A., 1906, i, 755; 1908, i, 422). As a result of further work, the authors now assign the constitution

$$CPh_2<\begin{matrix}C_6H_4\\ O\text{---}\end{matrix}>C(OH)\cdot C_6H_4\cdot NMe_2$$

to the compound, m. p. 194°, obtained by the action of excess of magnesium phenyl bromide on the isomeric methyl *p*-dimethylamino-*o*-benzoylbenzoates. This compound gives a *sulphate*,

$$C_{28}H_{25}O_2N,H_2SO_4,H_2O,$$

m. p. 140—150°; a *hydrochloride*, $C_{28}H_{25}O_2N,HCl,H_2O$, m. p. 140—150°; and a *platinichloride*, m. p. 190—200°. With hydroxylamine it gives a *compound*, $C_{28}H_{26}O_2N_2$, m. p. 179° (decomp.). The dimethylaminodiphenylanthracene obtained by the action of concentrated sulphuric acid on *p*-dimethylamino-o-benzhydryltriphenylcarbinol, when reduced by sodium amalgam in methyl-alcoholic solution, gives 10-*phenyl*-9-p-*dimethylaminophenyl*-9 : 10-*dihydroanthracene*, $CHPh<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CH\cdot C_6H_4\cdot NMe_2$, m. p. 184°. *p*-Dimethylamino-*o*-benzhydryltriphenylcarbinol condenses with dimethylaniline, yielding p-*dimethylaminobenzhydryl*(*diphenyl*-p-*dimethylaminobenzyl*)*benzene*,

$$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot CPh_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 122°, and with diethylaniline, giving p-*dimethylamino-benzhydryl*(*diphenyl*-p-*diethylaminobenzyl*)*benzene*, m. p. 128°. 1-Hydroxy-2 : 2-diphenyl-1-*p*-dimethylaminophenyl-1 : 2-dihydro*iso*-benzofuran also condenses with dimethyl- and diethyl-aniline. With the former it gives 2 : 2-*diphenyl*-1 : 1-*di*-p-*dimethylamino-phenyl*-1 : 2-*dihydro*iso*benzofuran*, $CPh_2<\begin{matrix}C_6H_4\\ O\text{---}\end{matrix}>C(C_6H_4\cdot NMe_2)_2$, occurring intwo crystalline forms: (1) prisms, m. p. 160°; (2) long needles, m. p. 166°. This compound when reduced with zinc and acetic acid yields o-*phenylbenzyldi*(-p-*dimethylamino*)*triphenyl-methane*, $CHPh_2\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$, m. p. 225°. With diethylaniline, the product of condensation is 2 : 2-*diphenyl*-1-p-*dimethylaminophenyl*-1-p-*diethylaminophenyl*-1 : 2-*dihydro*iso*benzo-furan*, m. p. 150°. These condensation products when heated with concentrated sulphuric acid yield the following anthracene deriv-

atives: 10-*hydroxy*-10-*phenyl*-9 : 9-*di*(-p-*dimethylaminophenyl*)-9 : 10-*dihydroanthracene*, $HO\cdot CPh<\substack{C_6H_4\\C_6H_4}>C(C_6H_4\cdot NMe_2)_2$, m. p. 228°, which with dimethylaniline yields 10-*phenyl*-9 : 9 : 10-*tri*(-p-*dimethylaminophenyl*)-9 : 10-*dihydroanthracene*, m. p. 264°, with diethylaniline, the corresponding 10-*phenyl*-9 : 9-*di*(-p-*dimethylaminophenyl*)-10-p-*diethylaminophenyl*-9 : 10-*dihydroanthracene*, m. p. 260°, with hydrochloric acid in methyl alcohol the 10-*methyl ether*, m. p. 175°, and in ethyl alcohol the 10-*ethyl ether*, m. p. 170°, and on reduction with zinc and acetic acid, 10-*phenyl*-9 : 9-*di*(-p-*dimethylaminophenyl*)-9 : 10-*dihydroanthracene*, m. p. 283°. The condensation product, m. p. 150°, from diethylaniline with concentrated sulphuric acid yields 10-*hydroxy*-10-*phenyl*-9-p-*dimethylaminophenyl*-9-*diethylaminophenyl*-9 : 10-*dihydroanthracene*, m. p. 214°.

A similar series of reactions has been carried out starting with methyl *p*-diethylamino-*o*-benzoylbenzoate, and the following compounds have been prepared:

1-*Hydroxy*-1-p-*diethylamino*-2 : 2-*diphenyl*-1 : 2-*dihydro*iso*benzofuran*, m. p. 160°, giving a *methyl ether*, m. p. 138—139°, an *ethyl ether*, m. p. 118°, and with hydroxylamine a *compound*, $C_{30}H_{30}O_2N_2$, m. p. 205°.

p-*Diethylamino*-o-*benzhydryltriphenylcarbinol*,

$$HO\cdot CPh_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NEt_2,$$

m. p. 140°.

2 : 2-*Diphenyl*-1 : 1-*di*(-p-*diethylaminophenyl*)-1 : 2-*dihydro*iso*benzofuran*, m. p. 163°.

2 : 2-*Diphenyl*-1-p-*diethylaminophenyl*-1-p-*dimethylaminophenyl*-1 : 2-*dihydro*iso*benzofuran*, m. p. 150°.

10-*Hydroxy*-10-*phenyl*-9 : 9-*di*(-p-*diethylaminophenyl*)-9 : 10-*dihydroanthracene*, $HO\cdot CPh<\substack{C_6H_4\\C_6H_4}>C(C_6H_4\cdot NEt_2)_2$, m. p. 225°.

10-*Phenyl*-9 : 9-*di*(-p-*diethylaminophenyl*)-10-p-*diethylaminophenyl*-9 : 10-*dihydroanthracene*, m. p. 258°.

10-*Phenyl*-10-p-*dimethylaminophenyl*-9 : 9-*di*(-p-*diethylaminophenyl*)-9 : 10-*dihydroanthracene*, m. p. 220°.

That the above anthracene derivatives have the constitution assigned to them was shown by the fact that tetramethyldiaminodiphenylanthrone when acted on with magnesium phenyl bromide yielded 10-hydroxy-10-phenyl-9 : 9-di(-*p*-dimethylaminophenyl)-9 : 10-dihydroanthracene, agreeing in its chemical and physical properties with the same compound described above.

When methyl *p*-dimethylamino-*o*-benzylbenzoate is acted on with magnesium phenyl bromide, it yields p-*dimethylaminobenzyltriphenylcarbinol*, $HO\cdot CPh_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2$, m. p. 139°, and p-*dimethylaminobenzylbenzopinacone*,

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 210° (decomp.). The carbinol when heated with sulphuric acid yields the *compound*, $C_{28}H_{26}ON\cdot SO_3H$, m. p. 240° (decomp.). With hydrogen chloride in benzene solution it yields the *compound*, $C_{28}H_{26}NCl$, m. p. 149°, and it gives a *platinichloride*, m. p.

180° (decomp.). When oxidised with chloroanil, the carbinol gives 1-hydroxy-2 : 2-diphenyl-1-*p*-dimethylaminophenyl-1 : 2-dihydro*iso*-benzofuran, already prepared from methyl dimethylaminobenzoylbenzoate. When condensed with dimethylaniline, the carbinol yields *o*-phenylbenzyldi(-*p*-dimethylamino)triphenylmethane, m. p. 225°, described above, which when oxidised with chloroanil gives a *compound*, $(C_{36}H_{36}ON_2)_2,C_6Cl_4O_2$, m. p. 180° (decomp.), which is converted by alcoholic potassium hydroxide into o-*phenylbenzyldi*(-p-*dimethylamino*)*triphenylcarbinol*,

$$CHPh_2{\cdot}C_6H_4{\cdot}C(OH)(C_6H_4{\cdot}NMe_2)_2,$$

m. p. 189°, giving a *hydrochloride*, m. p. 160—170° (decomp.). The original carbinol when condensed with diethylaniline gives o-*phenylbenzyl*-p-*diethylamino*-p-*dimethylaminotriphenylmethane*, $CHPh_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NEt_2){\cdot}C_6H_4{\cdot}NMe_2$, m. p. 150°, giving a *hydrochloride*, m. p. 170° (decomp.).

The *p*-dimethylaminobenzylbenzopinacone when heated with dilute sulphuric acid gives p-*dimethylaminobenzylbenzoylbenzene*, $COPh{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe_2$, m. p. 69°, and this compound is also obtained if the sulphuric acid is replaced by benzoyl chloride or dimethylaniline, or if the pinacone is heated alone.

Methyl *p*-diethylamino-*o*-benzylbenzoate when treated with magnesium phenyl bromide only gives one compound, namely, p-*diethylaminobenzyltriphenylcarbinol*,

$$HO{\cdot}CPh_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NEt_2,$$

m. p. 114°, which with dimethylaniline gives *o*-phenylbenzyl-*p*-diethylamino-*p*-dimethylaminotriphenylmethane, m. p. 150 (see above).

In a further endeavour to confirm the constitution of some of the compounds described above, the author has studied the action of magnesium phenyl bromide on 3-dimethylaminoanthraquinone. If an excess of the anthraquinone is used, the product is 3-*dimethylamino*-9(or 10)-*phenyloxanthranol*, $C_6H_4{<}{\substack{CPh(OH)\\CO}}{>}C_6H_3{\cdot}NMe_2$, m. p. 270°, which gives a *methyl ether*, m. p. 183°, an *ethyl ether*, m. p. 169°, and condenses with dimethylaniline, giving 3-*dimethylamino*-9 : 9(or 10 : 10)-*dimethylaminodiphenylanthrone*,

$$C_6H_4{<}{\substack{CPh(C_6H_4{\cdot}NMe_2)\\CO}}{>}C_6H_3{\cdot}NMe_2,$$

m. p. 205°. With an excess of magnesium phenyl bromide, the anthraquinone yields 3-*dimethylamino*-9 : 10-*diphenylanthracene*, $C_6H_4{<}{\substack{CPh\\CPh}}{>}C_6H_3{\cdot}NMe_2$, m. p. 264°, which when reduced with sodium amalgam in alcoholic solution gives 3-*dimethylamino*-9 : 10-*diphenyldihydroanthracene*, $C_6H_4{<}{\substack{CHPh\\CHPh}}{>}C_6H_3{\cdot}NMe_2$, m. p. 240°.

W. G.

Syntheses by means of Sodamide. Preparation and Study of New Mono- and Di-ketones. PHILIPPE DUMESNIL (*Ann. Chim.*, 1917, [ix], **8**, 70—116).—For the most part a résumé

of work already published (compare A., 1911, i, 718; 1913, i, 877). The following new compounds are described: *methylpropylacetophenone*, $CHMePr^{\alpha}\cdot COPh$, b. p. 244°/760 mm., 128°/15 mm., giving an *oxime*, m. p. 76°; *α-phenyl-β-methylbutyl alcohol*, $CHMeEt\cdot CHPh\cdot OH$, b. p. 120°/13 mm., giving an *acetate*, b. p. 123°/10 mm.; *α-phenyl-β-methylpentyl alcohol*,

$$CHMePr^{\alpha}\cdot CHPh\cdot OH,$$

b. p. 126—127°/12 mm., giving an *acetate*, b. p. 136°/13 mm.; *α-phenyl-β-ethylpentyl alcohol*, $CHEtPr^{\alpha}\cdot CHPh\cdot OH$, b. p. 134°/11 mm., giving an *acetate*, b. p. 144°/12 mm. *Methylethylacetophenoneoxime*, m. p. 82°; *ethylpropylacetophenoneoxime*, b. p. 150°/25 mm. *Benzylmethylpropylacetophenone*,

$$CH_2Ph\cdot CMePr^{\alpha}\cdot COPh,$$

b. p. 235°/40 mm. *β-Benzylbutane*, $CH_2Ph\cdot CHMeEt$, b. p. 102°/15 mm. *α-Benzyl-α-methylvaleramide*, $CH_2Ph\cdot CMePr^{\alpha}\cdot CONH_2$, m. p. 81°, giving the corresponding *acid*, m. p. 47°. *β-Benzylpentane*, $CH_2Ph\cdot CHMePr^{\alpha}$, b. p. 110°/25 mm. W. G.

Alkylated Indones. R. Stoermer and E. Laage (*Ber.*, 1917, **50**, 981—989).—A number of alkylated indones have been prepared by dissolving the *allo*-modifications of some alkylcinnamic acids in sulphuric acid containing a little anhydride and pouring the product on ice. The indones are accompanied by the stable forms of the acids, but can be separated by extraction from alkaline solutions. They are highly coloured oils, and usually possess very pungent odours, reminiscent of acraldehyde, which they also resemble in changing into resinous and solid polymerides when kept.

allo-β-Methylcinnamic acid yields 3-*methylindone*, b. p. 140—141°/19 mm., which forms a yellow *semicarbazone*, m. p. 208—216° (decomp.), and reacts with bromine in carbon disulphide to give a di-substitution product, namely, 2:6(?)-*dibromo*-3-*methylindone*, in orange-coloured needles, m. p. 157—157·5°. 3-*Ethylindone*, b. p. 158—159°/20 mm., m. p. 43·5°, yields a *semicarbazone*, lemon-yellow leaflets, m. p. 177·5°, and combines with bromine to form 2:3:6(?)-*tribromo*-3-*ethylhydrindone*,

$$C_6H_3Br{<}{\substack{CO\text{———}\\ CEtBr}}{>}CHBr,$$

which crystallises in colourless leaflets, and changes when heated into 2:6(?)-*dibromo*-3-*ethylindone*, orange-coloured leaflets, m. p. 108·5°.

2-Methylindone (A., 1915, i, 685) reacts with magnesium methyl iodide to form 1:2-*dimethylinden*-1-*ol*, $C_6H_4{<}{\substack{\text{——}CMe\cdot OH\\ CH{:}CMe}}$, which crystallises in small, quadratic leaflets, m. p. 82—82·5°, b. p. 117°/9 mm., and may be reduced to 1:2-*dimethylindan*-1-*ol* (1-*hydroxy*-1:2-*dimethylhydrindene*), m. p. 39—40°, b. p. 108·5°/8 mm. This carbinol is more easily obtained from 2-methylhydrindone, as this is readily prepared from β-phenyl-α-methylpropionyl chloride. It

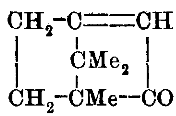
gives various colour reactions with sulphuric and nitric acids, and very readily loses the elements of water, for example, by boiling with 5% sulphuric acid, changing thereby into 2 : 3-*dimethylindene*. This is a pale yellow oil, m. p. 11°, b. p. 113—114°/21 mm., which forms an orange-red *picrate*, m. p. 86—87°.

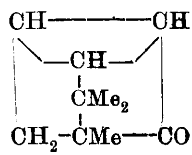
3-Methylindene is also more easily prepared by this scheme than by any other. Hydrindone is converted by the Grignard reaction into 1-hydroxy-1-methylhydrindene, m. p. 57° (A., 1913, i, 1364), and this is boiled with dilute sulphuric acid. J. C. W.

Action of Organo-magnesium Compounds on, and Reduction of, Cineol. C. F. VAN DUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 66—68).—Cineol gives an additive compound with magnesium methyl iodide, which when heated at 160° decomposes violently with vigorous evolution of a gas, and a liquid distils over (compare Grignard, *Bull. Soc. chim.*, 1903, [iii], **29**, 944). This liquid is now shown to be a mixture of hydrocarbons, b. p. 170—178°/759 mm., having the composition $C_{10}H_{16}$. It can be separated into three fractions, having (1) b. p. 170—172·5°, D^{16} 0·841; n_D^{16} 1·4679; (2) b. p. 172·5—175°, D^{16} 0·846, n_D^{16} 1·4706; (3) b. p. 175—178°, D^{16} 0·853, n_D^{16} 1·4752. A similar, but less vigorous, reaction takes place with magnesium ethyl bromide. With magnesium phenyl bromide the action is quite different, the additive compound not being decomposed by heat.

Attempts to reduce cineol by passing its vapour along with hydrogen over finely divided nickel at 170° were not successful. W. G.

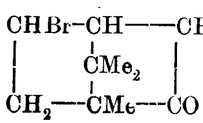
β-*pericyclo*Camphanone [Angeli's Camphenone, Schiff's Dehydrocamphor]. J. BREDT and WILHELM HOLZ (*J. pr. Chem.*, 1917, [ii], **95**, 133—159).—The substance obtained by Schiff (A., 1882, 527) and Angeli (A., 1895, i, 61, 382) by the elimination of a molecule of nitrogen from diazo-camphor was regarded by the latter investigator as camphenone of structure I, but evidence is now adduced in support of formula II, for which the descriptive name β-*pericyclo*camphanone is suggested; the term *peri* is used in analogy with the structure of naphthalene, indicating the position of the bridge which completes the trimethylene ring, this position being still further defined by the letter β :


(I.)

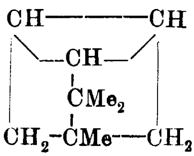

(II.)

β-*pericyclo*Camphanone (*semicarbazone*, needles, m. p. 243—244°) was prepared from camphorquinone by successive conversion into camphorquinone hydrazone (Forster and Zimmerli, T., 1910, **97**, 2156) and diazo-camphor, the liberation of nitrogen from the last

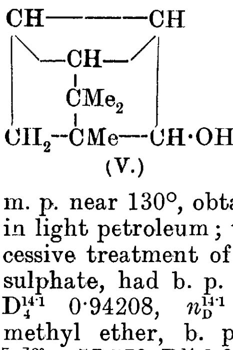
substance being aided by the presence of copper-bronze powder. In acetic acid solution it gradually formed a *hydrobromide* (annexed formula, III), m. p. 113—114°, $[\alpha]_D^{15}$ +13·23° in benzene, which on reduction yielded ordinary camphor. Contrary to Angeli's views, β-*pericyclo*camphanone does not react with bromine in carbon disulphide or chloroform, except under the influence of sunlight.


(III.)

By conversion of β-*pericyclo*camphanone into its *hydrazone*, m. p. near 45°, b. p. 143—148°/33 mm., and subsequent decomposition with alcoholic sodium ethoxide at 190°, pericyclo*camphane* (annexed formula, IV.), m. p. 117—118°, b. p. 150—152°, was obtained as an optically inactive substance which did not react with bromine in carbon disulphide or chloroform, and is possibly identical with Wagner's β-bornylene.


(.V.)

The reduction product of β-*pericyclo*camphanone with sodium and alcohol was not borneol, as Angeli believed, but an isomeric β-pericyclo*camphanol*, m. p. 174—176°, b. p. 205—208°, $[\alpha]_D^{20}$ +39·69° in benzene (annexed formula, V.); *phenylurethane*, $C_{10}H_{15}\cdot O\cdot CO\cdot NHPh$, needles, m. p. 106—108°; *methyl xanthate* derivative, $C_{10}H_{15}\cdot O\cdot CS_2Me$, colourless needles, m. p. 49—51°; *chloride*, $C_{10}H_{15}Cl$, m. p. near 130°, obtained by the action of phosphorus pentachloride in light petroleum; the *methyl ether*, $C_{10}H_{15}\cdot OMe$, prepared by successive treatment of the ethereal solution with sodium and methyl sulphate, had b. p. 189—190°, or 79—80°/16 mm., $[\alpha]_D^{20}$ +57·96°, $D_4^{14\cdot1}$ 0·94208, $n_D^{14\cdot1}$ 1·4654, and was quite distinct from *d*-bornyl methyl ether, b. p. 193—194°/760 mm., or 76—77°/14 mm., $[\alpha]_D^{20}$ +57·57°, D_4^{14} 0·9261, $n_D^{14\cdot1}$ 1·46479, the exaltation in the molecular refraction of the former substance being insufficient for the presence of an ethylenic linking and in accordance with the expected increment for a trimethylene ring.


(V.)

Confirmatory evidence of the presence of the trimethylene ring in β-*pericyclo*camphanone was obtained by the degradation of its *oxime*, tablets, the indefinite m. p., 80—127°, of which was probably due to the presence of stereoisomerides. When treated with diluted sulphuric acid and steam, the oxime yielded cyclo*campholenonitrile*, $CMe{<}{\begin{matrix}CH{-}CH\\ CMe_2\cdot CH\end{matrix}}{>}CH\cdot CN$, a viscid mass, m. p. 78—80°, b. p. 111—111·5°/17 mm., of unpleasant odour, which by prolonged treatment with alcoholic potassium hydroxide was convertible into the corresponding cyclo*campholenic acid*, $C_{10}H_{14}O_2$, leaflets, m. p. 108—110°; *ethyl* ester, b. p. 111—112°/14·5 mm., $[\alpha]_D^{11\cdot5}$ −105·98°, $D_4^{11\cdot4}$ 0·97936, $n_D^{11\cdot4}$ 1·47376, the spectrochemical characteristics of which were in accord with the presence of the trimethylene ring and the double bond. Oxidation of the *cyclo*campholenic acid with

potassium permanganate in neutral solution gave rise to cycloiso-*camphoronic acid*, $\begin{matrix} CH(CO_2H) \\ | \\ CH(CO_2H) \end{matrix}\!\!>CH \cdot CMe_2 \cdot CO_2H$, crystalline scales, m. p. 228—230°.

The constitution now suggested for β-*pericyclo*camphanone also gains probability from structural considerations, which indicate a difficulty in the formation of a double bond at either of the carbon atoms common to the two ring systems of the camphor molecule.

D. F. T.

Cerebrosides. III. Conditions for Hydrolysis of Cerebrosides. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, **31**, 627—634).—For the estimation of the sugar in a cerebroside, the most favourable conditions for hydrolysis seem to be to heat 1 gram of the cerebroside with 16 c.c. of 3% sulphuric acid with shaking in a sealed tube for twelve hours at 105°. Approximately 90% of the sugar present in the cerebroside is thus obtained. When the base and fatty acids are to be estimated, the heating should be continued for twenty-four hours. Detailed instructions are given for the isolation of cerebronic and lignoceric acids from the resulting hydrolytic products.

H. W. B.

Cerebrosides. IV. Kerasin. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1917, **31**, 635—647. Compare this vol., i, 525).—The authors have prepared and examined the acetyl, benzoyl, cinnamoyl, and *p*-nitrobenzoyl derivatives of phrenosin and kerasin with the view of employing them for the separation of these cerebrosides.

Hexa-acetylphrenosin, $C_{60}H_{105}O_{15}N$, has m. p. 41—43°, $[\alpha]_D^{20}$ −11·07°; Thierfelder (A., 1914, i, 339) gives m. p. 39—41°, $[\alpha]_D^{17}$ −3°. Penta-acetylkerasin, $C_{57}H_{101}O_{13}N$, melts at 54—56°, $[\alpha]_D^{20}$ −16·46°. Tribenzoylphrenosin, $C_{69}H_{105}O_{12}N$, is prepared by the action of benzoyl chloride on phrenosin in pyridine solution. It is obtained in crystalline form from methyl alcohol, m. p. 65—66°, $[\alpha]_D^{20}$ +21·2°. On decomposing with sodium methoxide, phrenosin is readily obtained. *Tricinnamoylphrenosin*, $C_{75}H_{111}O_{12}N$, and *tri-p-nitrobenzoylphrenosin*, $C_{69}H_{102}O_{28}N_4$, are prepared in a similar way. The former has m. p. 69—70°, $[\alpha]_D^{20}$ +21·72°, and the latter m. p. 94—96°, $[\alpha]_D^{20}$ +12·18°.

H. W. B.

Cerebrosides. V. Cerebrosides of the Kidney, Liver, and Egg Yolk. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1917, **31**, 649—654. Compare this vol., i, 525).—The composition of the cerebrosides of the kidney, liver, and egg yolk seems to be identical with that of the cerebrosides obtained from the nerve tissue. They contain the same sugar, galactose, the same base, sphingosine, and the same fatty acids, lignoceric and cerebronic.

H. W. B.

Synthesis of Mandelonitrile-glucoside, Sambunigrin, and similar Substances. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1917, **50**, 1047—1069).—The discovery of more and more cyanogetic glucosides, in ever-widening botanical species, has led botanists and chemists to speculate on the rôle of hydrogen cyanide in nitro-

gen assimilation. The synthesis of such glucosides gains, thereby, added interest, and, after failing in the case of glycollic acid to reach a further stage than the production of the glucosidoglycollamide, $NH_2 \cdot CO \cdot CH_2 \cdot O \cdot C_6H_{11}O_5$ (A., 1911, i, 802), success has now been achieved in the case of mandelic acid. The chemical history of mandelonitrile-glucoside is reviewed.

Dry, molten ethyl *dl*-mandelate is shaken with acetobromoglucose and silver oxide and so converted into a mixture of the *ethyl tetra-acetylglucosidomandelates*, which crystallises in concentric groups of needles, with fluctuating m. p. (102—109°) and rotation ($[\alpha]_D$ $-33°$ to $-40°$). The mixture is converted into the un-acetylated amides by means of methyl-alcoholic ammonia, and these are separated by crystallisation from a mixture of pyridine and ethyl acetate. A pyridine compound of l-*mandelamideglucoside* crystallises out, and this loses pyridine in a warm vacuum desiccator and on solution in water, leaving the pure amide as a glassy mass. The *isomeride* is also a viscous mass. Both are converted into crystalline tetra-acetates by treatment with acetic anhydride and pyridine. l-*Tetra-acetylglucosidomandelamide* forms microscopic needles, m. p. 161° (corr.), $[\alpha]_D^{19}$ $-89{\cdot}53°$, in acetone, and the d-*isomeride*, $C_6H_7O_5Ac_4 \cdot O \cdot CHPh \cdot CO \cdot NH_2$, crystallises in felted needles, m. p. 136—137° (corr.), $[\alpha]_D^{18}$ $-16{\cdot}53°$, in acetone. These are dehydrated to the nitriles by warming with phosphoryl chloride. The *l*-tetra-acetylglucosidomandelonitrile is obtained in rosettes of long, flat needles, m. p. 139—140° (corr.), $[\alpha]_D^{25}$ $-24{\cdot}01°$, agreeing, therefore, with the tetra-acetate of natural *l*-mandelonitrileglucoside (see especially Power and Moore, T., 1909, **95**, 259), and the *d*-isomeride, prismatic needles, m. p. 125—126° (corr.), $[\alpha]_D^{22}$ $-52{\cdot}5°$, coincides with the tetra-acetate of sambunigrin.

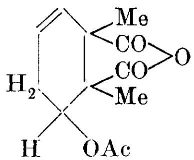
These tetra-acetates are hydrolysed by means of warm methyl-alcoholic ammonia, but racemisation takes place and the product is *dl*-mandelonitrile-glucoside, identical with natural prulaurasin (see especially Caldwell and Courtauld, T., 1907, **91**, 671). The mixture can be separated by crystallisation from a mixture of amyl alcohol and benzene (1 : 6). *d*-Mandelonitrile-glucoside, m. p. 151—152·5° (corr.), $[\alpha]_D^{15}$ $-76{\cdot}3°$, identical with sambunigrin (Bourquelot and Danjou, A., 1905, i, 912), crystallises out, and *l*-mandelonitrile-glucoside, m. p. 149—150° (corr.), $[\alpha]_D^{21}$ $-27{\cdot}0°$, may be recovered from the mother liquor. Both glucosides are hydrolysed under the influence of emulsin, which is surprising, unless it is due to the rearrangement of one into the other isomeride by the enzyme.

Amygdalin is easily acetylated by means of acetic anhydride and pyridine, and the hepta-acetate, m. p. 171—172° (corr.) (Caldwell and Courtauld, *loc. cit.*), may be hydrolysed to amygdalin again by means of methyl-alcoholic ammonia.

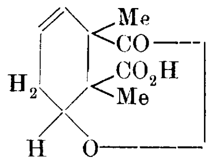
Glucosidoglycollamide (A., 1911, i, 802) may be converted by means of acetic anhydride and pyridine into a *tetra-acetate*, $C_6H_7O_5Ac_4 \cdot O \cdot CH_2 \cdot CO \cdot NH_2, H_2O$, m. p. 135—136°, and again at 155—156° (corr.), $[\alpha]_D^{20}$ $-23{\cdot}83°$, and this forms *tetra-acetylglucosidoglycollonitrile*, $C_6H_7O_5Ac_4 \cdot O \cdot CH_2 \cdot CN$, hexagonal plates, m. p. 129—130° (corr.), $[\alpha]_D^{18}$ $-38{\cdot}63°$, when warmed with phosphoryl

chloride. The acetate may be hydrolysed by means of methyl-alcoholic ammonia, but so far the expected glycollonitrile–glucoside has only been obtained as a syrup. J. C. W.

Cantharidin. VI. *iso*Cantharidin. J. Gadamer (*Arch. Pharm.*, 1917, **255**, 277—290. Compare Rudolph, this vol., i, 468). —The formula of cantharidin advocated by Rudolph (*loc. cit.*) explains all the known facts except two: first, the formation of α-hemimellitic acid by the pyrogenic decomposition of barium cantharate, and secondly, the properties of *iso*cantharidin and of *iso*cantharidic acid. The second discrepancy is now removed by the author's discovery that *iso*cantharidin and *iso*cantharidic acid do not exist, the substances described by Anderlini and Ghira in 1891 under these names being in reality *acetylhydratocantharic anhydride* (I) and *acetylhydratocantharic acid* respectively. The proof is



(I.)



(II.)

as follows. Accepting Rudolph's formula of cantharidin, cantharic acid must have formula II. *d*-Cantharic acid, $[\alpha]_D$ +87·5—90°, was heated with acetyl chloride at 135° for three hours. The yield of the resulting "*iso*cantharidin" was 120% of the theoretical, calculated on the formula $C_{10}H_{12}O_4$, and about 100% calculated on the formula $C_{12}H_{14}O_5$. The product after removal of a little *d*-cantharic acid, had $[\alpha]_D$ −100 to −101·25° in acetone ($c=2$), and in its other properties agreed with Anderlini and Ghira's "*iso*cantharidin," except that the m. p. was 84—85°, sintering at 80·5°. It contains one acetyl group and behaves like an acid anhydride during titration. It readily combines with $1H_2O$, yielding acetylhydratocantharic acid, which behaves as a dibasic acid and readily reverts to the anhydride by loss of water.

Anderlini and Ghira state that the barium salt is a specially characteristic derivative of "*iso*cantharidin." The author has therefore prepared this derivative of his lævorotatory compound, and finds that its properties agree with those recorded by Anderlini and Ghira; the analytical data, however, correspond with the formula $C_{12}H_{14}O_6Ba,3H_2O$, not with $C_{10}H_{12}O_5Ba,5H_2O$.

Danckwortt has observed (*Arch. Pharm.*, 1914, **252**, 680) that the product of the hydrolysis of "*iso*cantharidin" (acetylhydratocantharic anhydride) is not pure *d*-cantharic acid, since the $[\alpha]_D$ value is only +60·7 to +60·8°. The author shows that this is due to incomplete hydrolysis; when *l*-acetylhydratocantharic anhydride is hydrolysed by boiling water for several days the only product which can be isolated is *d*-cantharic acid, $[\alpha]_D$ +87·5°. C. S.

Cantharidin. VII. Reduction Products of Cantharic Acid and Hydrobromocantharic Acid. J. Gadamer (*Arch. Pharm.*, 1917, **255**, 290—302).—In consequence of the genetic

relationships recorded in this paper, the author re-names *d*-cantharic acid ($[\alpha]_D$ +87·5° to 90°) *l*-cantharic acid.

When *l*-cantharic acid dissolved in rather more than the calculated quantity of sodium carbonate solution is reduced by Mannich's modification of the Paal-Skita method, only one product is formed, namely, l-*dihydrocantharic acid*, $C_{10}H_{14}O_4$, m. p. 264—267°, $[\alpha]_D$ −52·5° in alcohol ($c=2$). The production of only one acid is regarded by the author as evidence in favour of the constitution of *l*-cantharic acid already recorded (preceding abstract), and therefore also of Rudolph's formula of cantharidin.

r-Cantharic acid, when reduced by the Paal-Skita method, yields r-*dihydrocantharic acid*, $C_{10}H_{14}O_4,\frac{1}{4}H_2O$, m. p. 264·5—265°, which can be partly resolved by means of the brucine salt; the *l*-acid thus obtained has $[\alpha]_D$ −33° to −35°. The same *l*-dihydrocantharic acid is obtained, together with a number of other, unexamined products, when *l*-hydrobromocantharic acid is reduced by zinc and hydrochloric acid.

When an alkaline solution of *l*-cantharic acid in aqueous sodium hydroxide is energetically reduced by hydrogen and palladium (on bone charcoal), *l*-dihydrocantharic acid and deoxycantharidin (or its hydrate, deoxycantharidic acid) are produced. The latter is optically inactive and agrees in all its properties with the deoxycantharidin obtained from the "dibromide" by Rudolph (this vol., i, 468).

The author has obtained evidence which seems to indicate the existence of a second modification of deoxycantharidin, which is amorphous, sinters strongly at 100°, and is completely molten at about 115°. C. S.

Bixins. I. J. Rinkes and J. F. B. van Hasselt (*Chem. Weekblad*, 1917, **14**, 888—894. Compare A., 1916, i, 425, 829).—One of the decomposition products of methylbixin ozonide is a liquid of agreeable odour, b. p. 52—60°/9 mm. It yields a *monosemicarbazone*, m. p. 261°; a *phenylosazone*, m. p. 170°; a *phenylmethylosazone*, m. p. 178°; a condensation *product* with Braun's reagent, m. p. 260°; and a *dioxime*, m. p. 187°. It is a dialdehyde of the formula $C_5H_6O_2$. The dibasic acid produced by oxidation with water and silver oxide is too soluble in water to admit of its extraction by ether.

Another decomposition product yields a *semicarbazone*, m. p. 218°, and a condensation *product* with Braun's reagent, m. p. 187°. It is an aldehyde of the formula $C_8H_{10}O_3$, and on oxidation is converted into a methoxy-*derivative*, $C_8H_{10}O_4$, m. p. 121°, which is the monomethyl ester of a dibasic *acid*, $C_7H_8O_4$, m. p. 231° (decomp.). On reduction by Paal and Skita's method, this acid takes up four hydrogen atoms, forming a compound, $C_7H_{12}O_4$, m. p. 93—94°, which is probably inactive β-methyladipic acid.

A. J. W.

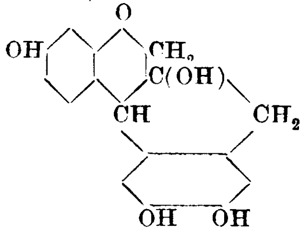
Pyrylium Compounds. III. W. Dilthey (*Ber.*, 1917, **50**, 1008—1010. Compare A., 1916, i, 829; *J. pr. Chem.*, 1917, [ii], **95**, 107).—The pyrylium compounds described in the earlier papers

were substituted in position 4. The cinnamylidene derivatives of ketones yield pyrylium compounds in which no substituent is present in this position. Thus, when a solution of phenyl cinnamylidenemethyl ketone in a mixture of acetic acid and acetic anhydride is boiled with ferric chloride, 2:6-*diphenylpyryl ferrichloride*, $CH{<}{\substack{CH:CPh\\CH\cdot CPh}}{>}OCl,FeCl_3$, is formed. This crystallises in yellow prisms, m. p. 185—186° (corr.), exhibits an intense blue fluorescence when dissolved in much acidified water, and yields 2:6-diphenylpyridine when treated with ammonia. Similarly, anisyl cinnamylidenemethyl ketone gives 2-*anisyl*-6-*phenylpyryl ferrichloride*, which crystallises in slender, brownish-yellow needles, m. p. 181° (corr.), and exhibits a strong, greenish-yellow fluorescence in solutions. A mixture of styryl phenyl ketone and styryl methyl ketone, under the same treatment, yields 6-*styryl*-2:4-*diphenylpyryl ferrichloride*, in reddish-yellow needles, m. p. 266° (corr.). J. C. W.

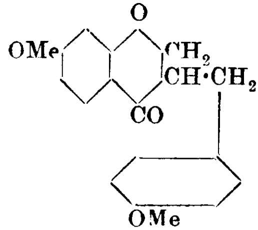
Action of Phthalic Anhydride on 1 : 6-Dihydroxynaphthalene. Formation of 6 : 6′-[3 : 11]-Dihydroxynaphthafluoran. II. O. FISCHER and E. KÖNIG (*Ber.*, 1917, **50**, 1011—1015. Compare A., 1914, i, 712).—During the preparation of 3:11-dihydroxynaphthafluoran by the condensation of phthalic anhydride and 1:6-dihydroxynaphthalene, a small quantity of an intermediate product, o-1:6-*dihydroxy*-2-*naphthoylbenzoic acid*, may be isolated, in very pale yellow needles or prisms, m. p. 220—221°. It may be converted by means of methyl sulphate into *methyl* o-1:6-*dimethoxy*-2-*naphthoylbenzoate*, m. p. 141—142°, and this hydrolysed to the free *acid*, m. p. about 214°.

3:11-Dihydroxynaphthafluoran reacts with the halogens in glacial acetic acid solution; the *dichloride*, $C_{28}H_{14}O_3Cl_2$, crystallises in colourless needles, decomp. 280°; the *dibromide* forms stellate groups of prisms, and the *di-iodide* is very similar. A *dinitro*-compound, yellow needles, has also been isolated. J. C. W.

Chromanones. The Brazilin Question. I. PAUL PFEIFFER and JOSEPH GRIMMER (*Ber.*, 1917, **50**, 911—927).—Pfeiffer is attempting to support his formula for brazilin (I) by synthesis, and has so far been able to prepare a compound of the formula II (compare *Chem. Zeitsch.*, 1904, **3**, 420; Perkin and Robinson, T., 1908, **93**, 493).



(I.)



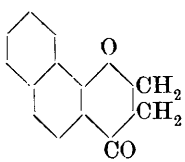
(II.)

The first stage consisted in the synthesis of 7-methoxychromanone, and as a preliminary attempt with this end in view, 2-hydroxy-4-methoxyacetophenone (pæonol) was condensed with formaldehyde in the presence of sulphuric acid. The product obtained, however, was 4 : 4′-*dihydroxy*-2 : 2′-*dimethoxy*-5 : 5′-*diacetyldiphenylmethane*, which crystallises in glistening needles, m. p. 197°, and forms a *dioxime*, m. p. 241° (decomp.), and a *diacetate*, m. p. 180°. *m*-Dimethoxybenzene behaves similarly with formaldehyde, yielding 2 : 2′ : 4 : 4′-*tetramethoxydiphenylmethane*, m. p. 149°.

The chromanone was finally obtained by reducing 7-methoxychromone by means of hydrogen and platinum-black. This compound is best obtained by Kostanecki's method (A., 1902, i, 304), and is characterised by a *semicarbazone*, m. p. 218° (decomp.). 7-*Methoxychromanone* [7-*methoxy*-2 : 3-*dihydro*-γ-*benzopyrone*], $OMe{\cdot}C_6H_3{<}\begin{matrix}O{-}CH_2\\ CO{\cdot}CH_2\end{matrix}$, crystallises in colourless needles, m. p. 58°, and forms a *semicarbazone*, m. p. 226—227° (decomp.), and an *oxime*, large needles, m. p. 137°. It also reacts with amyl nitrite and hydrochloric acid to form 3-*oximino*-7-*methoxychromanone* [3-*oximino*-7-*methoxy*-2 : 3-*dihydro*-γ-*benzopyrone*], a yellow powder, m. p. 169°, and it condenses with anisaldehyde to form the 3-*anisylidene* derivative. This crystallises in pale yellow, glistening leaflets, m. p. 134°, gives a deep orange-red solution in concentrated sulphuric acid, and may be reduced to 7 : 4′-*dimethoxy*-3-*benzylchromanone* [7 : 4′-*dimethoxy*-3-*benzyl*-2 : 3-*dihydro*-γ-*benzopyrone*], $OMe{\cdot}C_6H_3{<}\begin{matrix}O{-}CH_2\\ CO{\cdot}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe\end{matrix}$, leaflets, m. p. 68—70°.

Some chromanones of the naphthalene series have also been prepared.

α-Naphthachromone [α-naphtha-γ-pyrone] (Kostanecki, A., 1902, i, 303) is conveniently obtained by the condensation of 2-acetyl-α-naphthol with ethyl formate in the presence of powdered sodium. It crystallises in silky needles, m. p. 125°, forms a *semicarbazone*, m. p. 256° (decomp.), and may be reduced to α-*naphthachromanone* [2 : 3-*dihydro*-α-*naphtha*-γ-*pyrone*] (annexed formula). This crystallises in brilliant, rhombic, colourless tablets, m. p. 104·5°, which dissolve in sulphuric acid with a golden-yellow colour, and forms an *oxime*, m. p. 144—144·5°, a *semicarbazone*, m. p. 259—260° (decomp.), and a 3-*anisylidene* compound, pale yellow needles, m. p. 144—145°, which give a deep red solution in sulphuric acid.



Neither *ethyl* α-*naphthachromone*-2-*carboxylate* (pale brown, stout needles, m. p. 135°; for the acid, see *ibid.*) nor α-naphthaflavone, m. p. 167° (Kostanecki, A., 1898, i, 373), can be reduced by means of hydrogen and platinum-black.

2-Acetyl-α-naphthol condenses with anisaldehyde in the presence of sodium hydroxide to form 1-*hydroxy*-2-*naphthyl* p-*methoxystyryl*

ketone, orange-red needles, m. p. 160°, which may be reduced to 1-*hydroxy*-2-*naphthyl* β-p-*methoxyphenylethyl ketone*,

$$OH\cdot C_{10}H_6\cdot CO\cdot C_2H_4\cdot C_6H_4\cdot OMe,$$

very long, pale yellow needles, m. p. 114°. J. C. W.

Substituted Rhodanines and some of their Aldehyde Condensation Products. XIII. RUDOLF ANDREASCH (*Monatsh.*, 1917, **38**, 121—139).—The condensation of rhodanines and related ring systems with aldehydes is illustrated by still further examples (compare Stieger, this vol., i, 171).

3-Phenylrhodanine and *p*-aminobenzaldehyde condense in warm acetic acid to form 3-*phenyl*-5-p-*aminobenzylidenerhodanine*, $\begin{matrix} CS\text{---}S \\ | \\ NPh\cdot CO \end{matrix}\!\!>\!C{:}CH\cdot C_6H_4\cdot NH_2$, which crystallises in dichromate-coloured, filamentous needles, m. p. 227—228°, and dyes skin, wool, or silk yellow.

Phenylthiocarbimideglycollide and *p*-aminobenzaldehyde form *v-phenyl*-β-p-*aminobenzylidenethiocarbimideglycollide* [2 : 4-*diketo*-3-*phenyl*-5-p-*aminobenzylidenethiazolidine*],

$$\begin{matrix} CO\text{---}S \\ | \\ NPh\cdot CO \end{matrix}\!\!>\!C{:}CH\cdot C_6H_4\cdot NH_2,$$

as a yellow, crystalline powder, m. p. 246°. The corresponding *benzylidene* compound forms colourless needles, m. p. 239°, and the o-*hydroxybenzylidene* compound crystallises in pale yellow, woolly masses, m. p. 140°.

Phenylthiohydantoin yields *v-phenyl*-β-*benzylidene*iso*thiohydantoin* [2-*imino*-4-*keto*-3-*phenyl*-5-*benzylidenethiazolidine*], m. p. 255—256°, which has the appearance of lead iodide. The corresponding *salicylidene* compound has m. p. 244°.

Protocatechualdehyde and 3-phenylrhodanine form 3-*phenyl*-5-mp-*dihydroxybenzylidenerhodanine*, in bright yellow needles, m. p. above 260°. This behaves like an indicator, for aqueous suspensions give very deep violet solutions with alkali hydroxides, which become yellow again on neutralisation. The compound is in many other respects like alizarin; it is a vat dye, but does not give nice shades. The corresponding 5-op-*dihydroxybenzylidene* compound is an orange-yellow, crystalline powder, m. p. about 350°, which gives carmine-red solutions with traces of alkali hydroxide. 3-*Tolyl*-5-op-*dihydroxybenzylidenerhodanine* is a dirty orange-yellow powder, m. p. about 200°, and the corresponding 3-β-*naphthyl* compound has m. p. 190—200°.

3-Phenylrhodanine and *iso*phthalaldehyde condense to form 5-iso-*phthalylidene-bis*-3-*phenylrhodanine*,

$$\begin{matrix} CS\text{---}S \\ | \\ NPh\cdot CO \end{matrix}\!\!>\!C{:}CH\cdot C_6H_4\cdot CH{:}C\!<\!\!\begin{matrix} S\text{---}CS \\ | \\ CO\cdot NPh \end{matrix},$$

which crystallises from ethyl benzoate in chrome-yellow crusts, m. p. above 360°. The simple rhodanine gives the corresponding 5-iso-*phthalylidene-bis-rhodanine*, m. p. 260—265° (decomp.).

3-*Phenyl*-5-m-*carboxybenzylidenerhodanine* is a cadmium-yellow powder, m. p. 347—348° or higher.

Phenylrhodanine and the related ring systems also condense with isatin. 3-*Phenyl*-5-ψ-*indoxylidenerhodanine*,

$$\begin{matrix}\mathrm{CS{-}{-}S} \\ \mathrm{NPh \cdot CO}\end{matrix} > \mathrm{C{:}C} < \begin{matrix}\mathrm{CO} \\ \mathrm{NH}\end{matrix} > C_6H_4,$$

crystallises as a purple-red, shimmering scale, m. p. 260°. "iso*Thiohydantoin*-2-*indolindigo*" [2-*imino*-4-*keto*-5-ψ-*indoxylidenethiazolidine*], $\begin{matrix}\mathrm{NH{:}C{-}{-}S} \\ \mathrm{NH \cdot CO}\end{matrix} > \mathrm{C{:}C} < \begin{matrix}\mathrm{CO} \\ \mathrm{NH}\end{matrix} > C_6H_4$, is a brownish-red powder, m. p. above 360°. 2:4-*Diketo*-5-ψ-*indoxylidenethiazolidine* is an orange-yellow powder, m. p. above 370°. "5-ψ-Indoxylrhodanine" is identical with Felix and Friedländer's "5-thiazolthiol-2-indole-indigo" (A., 1910, i, 278). J. C. W.

A Theory of the Mechanism of the Phytochemical Synthesis of certain Alkaloids. Robert Robinson (T., 1917, **111**, 876—899).—Starting with ammonia, formaldehyde, ornithine, lysine, and degradation products of carbohydrates, it is shown how many alkaloids might be built up by reactions possible and probable to the living plant, namely, aldol condensations, and condensations of carbinol–amines containing the system $\mathrm{OH \cdot \dot{C} \cdot \dot{N}}$ with aldehydes or ketones, oxidations and reductions, eliminations of water, and methylations by means of formaldehyde. The theory is discussed with reference to the pyrrolidine, piperidine, quinuclidine, and *iso*quinoline (morphine, berberine, narcotine, corydaline, etc.) groups, and should stimulate chemists to much valuable work in these fields.

J. C. W.

Preparation of Compounds of Alkaloids of the Morphine Group. Soc. Chem. Ind. in Basle (Brit. Pat., 107409, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 979).—Alkaloids of the morphine group, or their derivatives, are caused to react in equimolecular proportions with CC-diallylbarbituric acid, a CC-allylalkylbarbituric acid, or a CC-dialkylbarbituric acid, giving well-crystallised compounds with valuable therapeutic (soporific or sedative) properties.

H. W.

Highly Active Vitamine Preparation thoroughly Freed from Inactive Ingredients. Soc. Chem. Ind. in Basle (U.S. Pat., 1235198, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 1064).—Organic food products are extracted with dilute alcohol and the alcohol removed from the extract by distillation in a vacuum. The aqueous solution of the extract is treated successively in acid condition with lead acetate and in neutral condition with basic lead acetate for the removal of impurities. After the solution has been freed from lead, it may be evaporated to dryness or may be first further purified by treatment with an alkaloid precipitant, decomposition of the precipitate, and re-solution of the alkaloid. The resulting vitamine products are yellowish-brown, hygroscopic substances, soluble in water-forming solutions faintly acid to litmus, and giving with

alkalis yellow solutions with a strong odour of methylamine. The aqueous solutions give precipitates with tannin, silver nitrate, and phosphomolybdic and phosphotungstic acids, the last of which gives characteristic colour reactions with sodium carbonate and diazobenzenesulphonic acid. H. W.

Syntheses by means of Sodamide. V. Preparation of δ-Aminoketones and of 2-Phenyl-3 : 3-dialkyltetrahydropyridines. A. HALLER and (MME.) RAMART-LUCAS (*Ann. Chim.*, 1917, [ix], **8**, 5—21).—The sodium derivatives of the dialkylacetophenones, COPh·CRR′Na, react with trimethylene chlorobromide, giving γ-chloropropyldialkylacetophenones, which with ammonia yield 2-phenyl-3 : 3-dialkyltetrahydropyridines. Thus, when ε-chloro-β-benzoyl-β-methylpentane (compare Haller and Bauer, A., 1911, i, 651) is heated in a sealed tube at 100° with alcoholic ammonia, it yields *2-phenyl-3 : 3-dimethyltetrahydropyridine*,

$$N{<}{\substack{CPh\cdot CMe_2\\ CH_2-CH_2}}{>}CH_2,$$

b. p. 150—151°/17 mm., a colourless liquid, which turns yellow in air. When heated with concentrated hydrochloric acid, this base gives *ε-amino-β-benzoyl-β-methylpentane hydrochloride*,

$$COPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2,HCl,$$

colourless prisms, m. p. 220°, giving a *platinichloride*. With dry hydrogen chloride in anhydrous ether, the tetrahydropyridine gives a *compound*, $C_{13}H_{18}NCl$, which is probably its hydrochloride.

When heated in a sealed tube at 100° with an alcoholic solution of dimethylamine, ε-chloro-β-benzoyl-β-methylpentane yields *ε-dimethylamino-β-benzoyl-β-methylpentane*,

$$COPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2,$$

b. p. 178—179°/18 mm., giving a *hydrochloride* and a *platinichloride*.

A similar series of compounds has been prepared from *ζ-chloro-γ-benzoyl-γ-methylhexane*, $COPh\cdot CMeEt\cdot CH_2\cdot CH_2\cdot CH_2Cl$, b. p. 175—180°/14 mm., of which the following are described: *2-phenyl-3-methyl-3-ethyltetrahydropyridine*, b. p. 160—161°/15 mm., giving a *hydrochloride*; *ζ-dimethylamino-γ-benzoyl-γ-methylhexane*, giving a *hydrochloride*, m. p. 120° (decomp.), and a *platinichloride*.

ζ-Chloro-γ-benzoyl-γ-ethylhexane yielded *ζ-amino-γ-benzoyl-γ-ethylhexane*, giving a *platinichloride*, and *ζ-dimethylamino-γ-benzoyl-γ-ethylhexane*, giving a *platinichloride*.

ε-Chloro-β-benzoyl-β-methylpentane will react with silver acetate instead of ammonia, giving *β-benzoyl-β-methylamyl acetate*, $COPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OAc$, which on hydrolysis gives the corresponding *keto-alcohol*, m. p. 120°. W. G.

The Compounds of Phenol and the Cresols with Pyridine. W. H. HATCHER and F. W. SKIRROW (*J. Amer. Chem. Soc.*, 1917, **39**, 1939—1977).—In the treatment of coal tar, it is already known that the crude phenols must be removed from the tar oils before the pyridine can be economically extracted with sulphuric acid

By experiment it is now shown that although in an equimolecular solution of pyridine and phenol in benzene the extraction of pyridine and phenol by dilute sulphuric acid and sodium hydroxide respectively is almost unaffected by the presence of the second solute, a quadrimolecular proportion of phenol very greatly reduces the extraction of pyridine by dilute sulphuric acid, although a quadrimolecular proportion of pyridine causes only a slight reduction in the percentage extraction of the phenol by dilute sodium hydroxide.

An examination of the compounds formed by pyridine with phenol, *o*-cresol, and *p*-cresol respectively, confirms the results already published by Bramley (T., 1916, **109**, 469). By cryoscopic investigation of equimolecular mixtures of pyridine with phenol, and of pyridine with *o*-cresol in solution in benzene or naphthalene, it is found that the compounds are considerably dissociated, the degree of dissociation increasing rapidly on dilution. Attempts are made to calculate the limits for this dissociation, taking into account the association of the compound and of its constituents.

D. F. T.

Ketens. XXIX. Comparison of Carbimides with Ketens. H. Staudinger and R. Endle (*Ber.*, 1917, **50**, 1042—1046).—Judging from their similarity in structure, ketens ($R\cdot CH{:}CO$ and $R_2C{:}CO$) and carbimides ($R\cdot N{:}CO$) should have certain reactions in common. For example, carbimides might be expected to unite with reactive unsaturated compounds to form derivatives of four-membered ring systems, which is a reaction given by ketens, especially those of the second type. Whilst they do not form such products at low temperatures, they do react at higher temperatures to give substances which can be interpreted as being degradation products of the additive compounds.

Phenylcarbimide reacts with *p*-dimethylaminobenzaldehyde at 190° to form *p*-dimethylaminobenzylideneaniline, thus:

$$NMe_2\cdot C_6H_4\cdot CHO + C_6H_5\cdot N{:}CO = \begin{array}{l} NMe_2\cdot C_6H_4\cdot CH{-}O \\ \qquad\qquad\quad\; | \qquad | \\ \qquad\qquad\quad NPh\cdot CO \end{array} \longrightarrow$$

$$NMe_2\cdot C_6H_4\cdot CH{:}NPh + CO_2.$$

With tetramethyldiaminothiobenzophenone at 170°, it yields phenylauramine and carbon oxysulphide, and with nitrosobenzene at 120° it forms azobenzene.

p-Methoxyphenylcarbimide and Michler's ketone yield *p-methoxyphenylauramine*, orange-red crystals, m. p. 172—173°, thus:

$$CO(C_6H_4\cdot NMe_2)_2 + OMe\cdot C_6H_4\cdot N{:}CO \longrightarrow \begin{array}{l} (NMe_2\cdot C_6H_4)_2C{-}O \\ \qquad\qquad\quad\;\; | \qquad | \\ OMe\cdot C_6H_4\cdot N{-}CO \end{array} \longrightarrow$$

$$(NMe_2\cdot C_6H_4)_2C{:}N\cdot C_6H_4\cdot OMe + CO_2.$$

p-Dimethylaminophenylcarbimide might be expected to be more reactive than phenylcarbimide, but it is less so. It is obtained as follows: methyl *p*-dimethylaminobenzoate is converted into *p-dimethylaminobenzhydrazide*, m. p. 170—171°, this into the

azide, $NMe_2\cdot C_6H_4\cdot CO\cdot N_3$, decomp. 97°, and this by heating into p-*dimethylaminophenylcarbimide*, m. p. 39°, b. p. 90—92°/abs. vac. The compound reacts with water to form tetramethyldiaminodiphenylcarbamide; with methyl alcohol it gives p-*dimethylaminophenylurethane* [*methyl* p-*dimethylaminophenylcarbamate*], m. p. 101—103°, and with aniline it yields p-*dimethylaminodiphenylcarbamide*, m. p. 207—208°. J. C. W.

Pyrimidines. LXXXV. Synthesis of a Secondary Nucleoside of Thymine and its Conversion into a Derivative of Glyoxaline by Hydrolysis with Acids. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1919—1927. Compare A., 1916, i, 754).—Ethyl β-keto-γ-ethoxy-α-methyl-n-valerate, $OEt\cdot CHMe\cdot CO\cdot CHMe\cdot CO_2Et$, in the presence of alcoholic sodium ethoxide undergoes condensation with thiocarbamide, with formation of 6-*oxy*-2-*thio*-5-*methyl*-4-α-*ethoxyethylpyrimidine*, $NH{<}\substack{CO\cdot CMe\\CS-NH}{>}C\cdot CHMe\cdot OEt$, colourless prisms, m. p. 222°, which reacts with ethyl chloroacetate and alcoholic sodium ethoxide, with formation of *ethyl* 6-*oxy*-5-*methyl*-4-α-*ethoxyethylpyrimidine*-2-*thiolacetate*, $NH{<}\substack{CO\text{———————}CMe\\C(S\cdot CH_2\cdot CO_2Et):N}{>}C\cdot CHMe\cdot OEt$, colourless prisms, m. p. 119°, and on treatment with aqueous chloroacetic acid suffers elimination of sulphur, with production of 2 : 6-*dioxy*-5-*methyl*-4-α-*ethoxyethylpyrimidine*, $NH{<}\substack{CO\cdot CMe\\CO-NH}{>}C\cdot CHMe\cdot OEt$, prisms, m. p. 176°. By a similar series of changes, starting with thiocarbamide and ethyl β-keto-γ-methoxy-α-methyl-n-valerate, there is obtained 6-*oxy*-2-*thio*-5-*methyl*-4-α-*methoxyethylpyrimidine*,

$$NH{<}\substack{CO\cdot CMe\\CS-NH}{>}C\cdot CHMe\cdot OMe,$$

which can be further converted into 2 : 6-*dioxy*-5-*methyl*-4-α-*methoxyethylpyrimidine*, $NH{<}\substack{CO\cdot CMe\\CO-NH}{>}C\cdot CHMe\cdot OMe$, prisms, m. p. 217°. On heating the dioxyethoxyethyl- or dioxymethoxyethylpyrimidine compound with hydrochloric or hydrobromic acid, decomposition is effected, with formation of methylethylglyoxalone, $\substack{CMe\cdot NH\\ \|\\ CEt-NH}{>}CO$, but with dioxymethylethoxyethylpyrimidine, using special precautions, a small quantity of the *thymine-nucleoside*, $NH{<}\substack{CO\cdot CMe\\CO-NH}{>}C\cdot CHMe\cdot OH$, m. p. 219—220°, is obtained; this is extremely unstable in the presence of hot acids and readily changes into the glyoxalone compound. D. F. T.

Acid Additive Compounds of Azobenzene-*p*-hydrazones. J. TRÖGER and J. PIOTROWSKI (*Arch. Pharm.*, 1917, **255**, 233—261).—The reaction between aromatic aldehydes and azobenzene-p-hydrazinesulphonic acids to form hydrazones having well-marked basic properties (Tröger and Müller, A., 1908, i, 1025;

Tröger and Puttkammer, A., 1909, i, 68, 69) has been extended to aliphatic aldehydes and ketones. The condensation proceeds even more easily in these cases, but the hydrazones are sometimes difficult to isolate on account of the solubility of the salts.

Equal molecular quantities of acetone and azobenzene-*p*-hydrazinesulphonic acid suspended in alcohol yield iso*propylideneazobenzene*-p-*hydrazone sulphate*, $N_2Ph{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CMe_2,H_2SO_4$, bluish-violet, crystalline powder, by warming with a drop of concentrated sulphuric acid on the water-bath for about fifteen minutes; the free *hydrazone*, $C_{15}H_{16}N_4$, obtained by means of 5% aqueous ammonia, forms dark brown needles, m. p. 111·5°. By a similar reaction in glacial acetic acid, acetylacetone and azobenzene-*p*-hydrazinesulphonic acid (2 mols.) yield the *sulphate*, violet-brown, crystalline powder, of *acetylacetonebisazobenzene*-p-*hydrazone*, $CH_2(CMe{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph)_2$, orange leaflets, m. p. 87°.

Azobenzene-*p*-hydrazinesulphonic acid and ethyl acetoacetate react in alcoholic hydrochloric acid, initially at 0° and finally on the water-bath, to form a mixture of a hydrochloride and a sulphate, from which 5% aqueous ammonia liberates the expected *hydrazone*, $N_2Ph{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et$, reddish-brown needles, m. p. 127°; the *hydrochloride*, $C_{18}H_{20}O_2N_4,HCl$, is a violet, crystalline powder. Chloroacetaldehyde hydrate and azobenzene-*p*-hydrazinesulphonic acid yield *chloroethylideneazobenzene*-p-*hydrazone sulphate*, $CH_2Cl{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph,H_2SO_4$, amorphous, black powder with green reflex, from which 5% aqueous ammonia liberates, not the hydrazone, but a *substance*, dark brown prisms, m. p. 200°. Dextrose and azobenzene-*p*-hydrazinesulphonic acid yield a *hydrochloride*, $C_{18}H_{22}O_5N_4,HCl$, steel-blue prisms, but the free hydrazone could not be isolated.

In addition to many already recorded (*loc. cit.*), the following salts are described: *benzylideneazobenzene*-p-*hydrazone hydriodide*, $CHPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph,HI$, blackish-violet, amorphous powder; p-*tolylideneazobenzene*-p-*hydrazone sulphate*, violet needles, and *hydrobromide*, dark violet powder; p-iso*propylbenzylideneazobenzene*-p-*hydrazone sulphate*, ultramarine needles; *cinnamylideneazobenzene*-p-*hydrazone hydrochloride* and *hydrobromide*, both black, crystalline powders; o-*chlorobenzylideneazobenzene*-p-*hydrazone*, brownish-red crystals, m. p. 150·5°, and its *sulphate*, dirty violet, amorphous powder, *hydrochloride*, brownish-violet powder, and *hydrobromide*, microcrystalline, brownish-black powder; p-*chlorobenzylideneazobenzene*-p-*hydrazone*, golden-yellow leaflets, m. p. 177°, and its *sulphate*, ultramarine crystals; o-*nitrobenzylideneazobenzene*-p-*hydrazone*, reddish-brown needles, m. p. 194° (from a little benzene), or brownish-black needles, m. p. 196° (from much benzene), and its *sulphate*, ultramarine needles, *hydrochloride*, greyish-violet needles, and *hydriodide*, brownish-black needles; p-*nitrobenzylideneazobenzene*-p-*hydrazone sulphate*, steel-blue needles; *salicylideneazobenzene*-p-*hydrazone hydrochloride*, moss-green needles, and *hydriodide*, olive-green, micro-

crystalline powder; p-*methoxybenzylideneazobenzene*-p-*hydrazone hydrochloride*, bluish-black needles; *furfurylideneazobenzene*-p-*hydrazone sulphate*, steel-blue, microscopic needles, *hydrochloride* and *hydrobromide*, blackish-violet, amorphous powders. C. S.

p-Chlorobenzeneazo-α-naphthylhydrazinesulphonic Acid. J. Tröger and J. Piotrowski (*Arch. Pharm.*, 1917, **255**, 157—171).—*p*-Chlorobenzeneazo-α-naphthylamine cannot be diazotised satisfactorily by any of the usual methods. The following method gives good results under the conditions stated. An emulsion of *p*-chlorobenzeneazo-α-naphthylamine and water (30 parts) is treated with 25% hydrochloric acid (10 mols.) and warmed at about 75° for a short time until the hydrochloride has been formed. The mixture is transferred to a pressure bottle, cooled to about 45°, powdered sodium nitrite (about 2 mols.) is added, the bottle is closed and shaken two or three times, not too violently, and the liquid is at once filtered rapidly, the process of diazotisation requiring only a few seconds. The bottle should be only partly filled, and only small quantities of material (6 grams) should be operated on. The *diazonium chloride*, $C_{16}H_{10}N_4Cl_2$, which separates from the filtrate in cherry-brown or brownish-red needles, is not explosive, and can be recrystallised from hot water, but the solid appears to lose nitrogen by prolonged keeping. It couples with β-naphthol in dilute aqueous sodium hydroxide to form p-*chlorobenzeneazo-α-naphthylazo-β-naphthol*,

$$C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH,$$

stellate, violet crystals with olive-green reflex, m. p. 261°, and with aniline in aqueous solution to form p-*chlorobenzeneazo-α-naphthylazoaniline*, $C_{22}H_{16}N_5Cl$, brown prisms or needles, m. p. 142°, and is converted by an alkaline solution of potassium sulphite into the metastable form of *potassium* p-*chlorlobenzeneazo-α-naphthyldiazosulphonate*, $C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot SO_3K$, pale brown flocks, which changes to the amorphous, coffee-brown, stable salt by keeping for a day in the mother liquor. The last-mentioned salt is reduced by ammonium sulphide (compare Tröger and Westerkamp, A., 1910, i, 207) to *potassium* p-*chlorobenzeneazo-α-naphthylhydrazinesulphonate*, $C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3K$, golden leaflets. The free *hydrazinesulphonic acid*, $C_{16}H_{13}O_3N_4ClS$, is a brownish-violet powder with olive-green reflex, which reacts in the presence of alcoholic hydrogen chloride with cinnamaldehyde and with salicylaldehyde to form *cinnamylidene*-p-*chlorobenzeneazo-α-naphthylhydrazone*, $C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot NH\cdot N{:}CH\cdot CH{:}CHPh$, deep cherry-red, stellate needles, m. p. 166° (decomp.), and *salicylidene*-p-*chlorobenzeneazo-α-naphthylhydrazone*, $C_{23}H_{17}ON_4Cl$, brown needles, m. p. 162° (decomp.), respectively.

The hydrazinesulphonic acid is reduced by zinc dust and 30% acetic acid, yielding ammonia, sulphuric acid, and *p*-chloroaniline, but the expected naphthylenediamine could not be detected.

C. S.

Structure of Yeast-nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1917, **31**, 591—598. Compare Jones and Read, this vol., i, 233).—The *brucine* salt of cytosine–uracil–dinucleotide melts at 200° (corr.), and, when treated with ammonia to remove the brucine and then with barium hydroxide, yields the *barium* salt of the same dinucleotide, $C_{18}H_{21}O_{16}N_5P_2Ba_2,2H_2O$, $[\alpha]_D^{25}$, in 2·5% hydrochloric acid solution, +12·5°.

The author directs attention to the possibility of the existence of six ways of linking between two nucleotides instead of only two, as hitherto assumed (*loc. cit.*). H. W. B.

Digestibility of Starches from various Vegetable Foods by the Diastases from Malt, Pancreas, and Saliva. MARIUS PAULETIG (*Zeitsch. physiol. Chem.*, 1917, **100**, 74—92).—The author incubates solutions of the various starches with diastases from different sources, and, after two hours, notes the behaviour of the mixtures to iodine and Fehling's solutions. The chief conclusion drawn by the author is that diastase hydrolyses starch from cereals more readily than starch from the leguminosæ. H. W. B.

Action and Occurrence of Arginase. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1917, **100**, 111—116).—The activity of arginase is increased in the presence of phosphates and inhibited by soluble calcium and magnesium salts.

Arginase is present in the human fœtal liver, but not in the kidney or small intestine. It could not be detected in yeast or in soja beans.

The specificity of arginase is illustrated by the fact that it does not liberate carbamide from either guanidinoacetic or guanidinopropionic acids. H. W. B.

Constitution of Hydrargyrum thymolo-aceticum. E. RUPP (*Arch. Pharm.*, 1917, **255**, 191—197).—The formula

$$OAc{\cdot}Hg{\cdot}O{\cdot}C_6H_3MePr,Hg(OAc)_2,$$

which has long been given to thymol-mercuric acetate, must certainly be incorrect, since the compound does not contain ionisable mercury. It is now found that the substance is 2 : 6-diacetatomercurithymol, $OH{\cdot}C_6HMePr(Hg{\cdot}OAc)_2$, since its mixture with glacial acetic acid and potassium nitrate is converted by sulphuric acid in the cold into 2 : 6-dinitrothymol. It is converted by hot 10% sodium hydroxide into the *sodium* derivative of 2 : 6-*dihydroxymercurithymol*, $C_{10}H_{13}O_3NaHg_2,3H_2O$, colourless plates, an aqueous solution of which is converted into the *anhydride*,

$$OH{\cdot}Hg{\cdot}C_6HMePr{<}\begin{matrix}Hg\\|\\O\end{matrix}{>},$$

by carbon dioxide, into 2 : 6-*dichloromercurithymol*, colourless crystals, by a saturated solution of sodium chloride, and into 2 : 6-*dinitratomercurithymol*, colourless crystals, by 5% nitric acid. 2 : 6-*Diiodomercurithymol* has also been prepared.

The mercury in organic substances can be estimated by heating

0·3 gram of the substance with 5 c.c. of sulphuric acid and 1 gram of potassium nitrate, boiling the solution for ten to thirty minutes until it is colourless, cooling, adding permanganate until a permanent pink coloration is obtained, and, after the addition of a drop of hydrogen peroxide, titrating with $N/10$-thiocyanate with iron alum as indicator. C. S.

Physiological Chemistry.

Capacity of Blood and Hæmoglobin to Unite with Carbon Dioxide. G. A. Buckmaster (*J. Physiol.*, 1917, **51**, 164—175).—Dialysed blood corpuscles have the power of absorbing carbon dioxide, and the author attributes this power to the hæmoglobin, since no other protein appears to be able to absorb carbon dioxide to the same degree. G. B.

Tables for Finding the Alkaline Reserve of Blood Serum, in Health and in Acidosis, from the Total Carbon Dioxide or the Alveolar Carbon Dioxide or the Hydrogen-ion Concentration at Known Carbon Dioxide Tension. J. F. McClendon, A. Shedlov, and W. Thomson (*J. Biol. Chem.*, 1917, **31**, 519—525. Compare McClendon, this vol., ii, 423).—Diagrams are given in the text by means of which it is possible to ascertain directly the alkaline reserve of the serum of the blood when the carbon dioxide or hydrogen-ion concentration of the serum under defined conditions has been estimated. The 'alkaline reserve' is defined by the authors as the difference between the sum of the equivalents of strong bases and the sum of the equivalents of strong acids in the serum, expressed as a fraction of a normal solution (compare Van Slyke and Cullen, this vol., i, 521). H. W. B.

Influence of Respiration on the Exchange of SO_4 between Corpuscles and Plasma, and its Effect on the Excretion of SO_4. S. de Boer (*J. Physiol.*, 1917, **51**, 211—220).—A quantity of carbon dioxide, passed into blood within physiological limits (15—20 vols. per cent.) causes SO_4 to leave the serum and to pass into the corpuscles, in which it is transported to the kidneys for excretion. Estimations of SO_4 in serum were carried out by measuring the height of the column of barium sulphate (after centrifuging in a hæmocrite) obtained from the ultra-filtrate. Normal serum contains 0·0212% SO_4. G. B.

The Chemistry and Physiology of the Coagulation of the Blood. III. E. Herzfeld and R. Klinger (*Biochem. Zeitsch.*, 1917, **82**, 289—309. Compare A., 1916, i, 613).—The following processes are assumed to take place in coagulation: (1) Prothrombin $\longrightarrow$ thrombin in the presence of calcium chloride, the

reaction (proteolysis) being accelerated by "activators." (2) Thrombin + fibrinogen = fibrin. Reasons are given for believing that the prothrombin is not a definite protein, neither is it derived from any particular species of blood cells. It is probably derived from various cells, and is found in the plasma in the form of higher degradation products of proteins. Experiments are described which tend to show that lipoids are not absolutely essential for the formation of thrombin from prothrombin, but that other substances can act as "activators" (accelerating proteolysis). The same remark applies to the higher fatty acids. The change into the so-called "metathrombin" (an inactive thrombin) is ascribed to an adsorption by the colloids of the serum. S. B. S.

Carbon Dioxide and the Coagulation of Blood. MARIO CHIÒ (*Arch. Farm. sperim.*, 1917, **23**, 202—224, 225—235; from *Chem. Zentr.*, 1917, ii, 62—63).—Three factors have previously been recognised as necessary for the coagulation of blood: (1) fibrinogen, which yields fibrin by the action of the fibrin enzyme; (2) a pro-enzyme; and (3) soluble and ionised salts of calcium which, by union with the pro-enzyme, yield the fibrin enzyme. According to the author's experiments on the plasma of rabbits and guinea-pigs, a fourth factor must be taken into account, namely, carbon dioxide, on the tension of which the equilibrium of the calcium salts, and consequently the possibility of their union with the pro-enzyme to enzyme, depends. The author considers that the difference in behaviour of blood withdrawn from the organism and blood in the body is caused by the former not being enclosed in a vessel made of living tissue and by being in contact with gases at a different tension. Efforts to provide a suitable substitute for the living tissue were unsuccessful. On the other hand, it was found possible to collect the blood in a vessel containing a mixture of oxygen and carbon dioxide in which the partial pressure of the latter could be maintained within the physiological limits (30—50 mm. mercury). A distinct change in the conditions of coagulation was then observed. Whilst, otherwise, blood coagulated within a few minutes in ordinary or paraffined glass vessels, guinea-pig blood was not completely coagulated within an hour in a paraffined vessel in an atmosphere of carbon dioxide (2 vols.) and oxygen (1 vol.) at a pressure of 50 mm. (partial pressure of carbon dioxide, 33·3 mm.), and rabbit's blood remained liquid after this period and was not entirely coagulated after four hours; even in ordinary glass vessels, coagulation did not commence in the latter case until after twenty-five minutes. After addition of salt, the plasma of either animal refused to coagulate in an atmosphere of carbon dioxide at 20—30 mm. pressure. It did not, however, lose its ability to coagulate, but the fibrin enzyme completely lost its activity, probably because it is a product of a balanced action in which carbon dioxide is one factor affecting the equilibrium. Calcium salts and carbon dioxide are mutually antagonistic.

H. W.

Metabolism of Arginine. III. Arginine and Creatine Formation. W. H. THOMPSON (*J. Physiol.*, 1917, **51**, 111—153).—A daily dose of 2 grams of arginine carbonate given to dogs by the mouth increases the creatine output by 10%, but this represents only a methylation of 2·5% of the guanidine nucleus given. In ducks, these figures are 22·6% and 1·1% respectively. When arginine is injected hypodermically, more (about twice as much) creatine is formed, than after administration by the mouth. After intravenous injection of arginine in rabbits, some creatine formed from it (8—25% of the guanidine nucleus) is stored in the muscles, at least temporarily, and some is at once excreted in the urine (about 1% during the first three hours after injection). The percentage figures for the excretion of arginine in dog's urine as total nitrogen, urea, ammonia, amino-acid, and total creatinine nitrogen are: for feeding, 56·5, 34·7, 13·7, 2·33, and 3·47 respectively, and for hypodermic injection, 67·87, 35·4, 4·05, 4·7, and 4·12 respectively. G. B.

Nutritive Value of Margarines and Butter Substitutes with Reference to their Content of the Fat-soluble Accessory Growth Substance. W. D. HALLIBURTON and J. C. DRUMMOND (*J. Physiol.*, 1917, **51**, 235—251).—The fat-soluble accessory growth substance of beef-fat and "oleo-oil" is present in margarines prepared on such a basis. Such margarines are nutritively equivalent to butter. Coconut oil, cotton-seed oil, Arachis oil, and hydrogenated vegetable oils contain little or none of this accessory substance. Margarines from these, and nut butters prepared from crushed nuts, are not equal to butter in nutritive value. Lard substitutes from vegetable oils are equal to lard in nutritive value, both alike being destitute of the fat-soluble accessory substance.
G. B.

Growth. IX. Influence of Tethelin on the Early Growth of the White Mouse. T. BRAILSFORD ROBERTSON and M. DELPRAT (*J. Biol. Chem.*, 1917, **31**, 567—574. Compare Robertson, A., 1916, i, 350).—The administration of tethelin (a lipoid extracted from the anterior lobe of the pituitary gland) to female mice does not have any appreciable effect on the growth of the suckling young. After the fourteenth day, when the eyes of the young mice are open and they have access to food other than that supplied to the mother, the administration of tethelin to the young animals results in a noticeable acceleration of growth during the second growth cycle (second to fifth weeks), which is followed by a marked retardation during the subsequent third growth cycle, even though the administration of tethelin is discontinued at the end of the fifth week. H. W. B.

Synthetic Sugar Formation in the Artificially Perfused Liver. II. KARL BALDES and FRITZ SILBERSTEIN (*Zeitsch. physiol. Chem.*, 1917, **100**, 34—53. Compare Embden, Schmitz, and Wittenberg, A., 1913, i, 1411).—The results of perfusion experiments

on the livers of phloridzinised dogs indicate that lactic acid is converted into dextrose with the intermediate formation of glyceraldehyde. The addition of glyceric or pyruvic acid or of glycollaldehyde to the perfusing fluid did not lead in any case to the formation of dextrose. H. W. B.

Factors Necessary for the Formation of Carbamide from Ammonia and Carbon Dioxide in the Isolated Liver. I. Behaviour of Ammonium Carbonate Circulated with Ringer's Solution through the Isolated Liver. ANTONIO CLEMENTI (*Arch. Farm. sperim.*, 1917, **33**, 289—304; from *Chem. Zentr.*, 1917, ii, 173—174).—It has been previously observed by Schröder that carbamide is formed when a solution of ammonium carbonate in defibrinated blood is circulated through the isolated liver; such formation does not occur when the defibrinated blood is replaced by Ringer's solution. In experiments with the liver of the dog, small quantities of carbamide were detected when ammonium carbonate was not added; after addition of this substance the amount of carbamide was only very slightly increased, and this result is probably attributable to a further action of liver arginase. The added ammonia is almost quantitatively recovered, partly from the solution and partly from the liver tissue. One or more components of defibrinated blood must therefore be necessary for the formation of carbamide. H. W.

Glycolytic Properties of Muscular Tissue. RALPH HOAGLAND and C. M. MANSFIELD (*J. Biol. Chem.*, 1917, **31**, 501—517).—When pieces of muscular tissue from the ox, freed from blood by draining, but not by washing out the vessels with water or saline solution, are incubated under strictly aseptic conditions, a disappearance of dextrose occurs without the production of an equivalent amount of carbon dioxide. The glycolysis takes place most rapidly during the first few hours after the death of the animal and then progresses at a slow rate for several days. In some cases a preliminary increase in the total carbohydrate is observed owing to the production of glycogen, which appears to indicate the existence of a capacity for synthesis as well as for catalysis of dextrose by the tissue enzymes. The formation of disaccharides was not detected (compare Levene and Meyer, A., 1912, ii, 577). H. W. B.

Chemistry of Lactacidogen. II. GUSTAV EMBDEN and FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1917, **100**, 181. Compare A., 1915, i, 345).—By treating an extract of muscle containing lactacidogen with phenylhydrazine, the crystalline phenylhydrazine salt of the phenylosazone of hexosephosphoric acid is obtained. Lactacidogen must therefore possess a structure similar to that of hexosephosphoric acid. H. W. B.

Function of Muscular Tissue in Urea Formation. RALPH HOAGLAND and C. M. MANSFIELD (*J. Biol. Chem.*, 1917, **31**,

487—499).—The amount of urea in muscular tissue does not alter during aseptic autolysis, indicating the absence of urease and of urea-forming enzymes, such as arginase. H. W. B.

[Selenium in Bones, Teeth, and Urine]. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1917, **100**, 182—189).—See this vol., ii, 540.

Specific Pigment-forming Ferment of the Skin, Dopaoxydase. BR. BLOCH (*Zeitsch. physiol. Chem.*, 1917, **100**, 226—254).—When a frozen section of human or other skin is treated with a 1°/₀₀ solution of 3:4-dihydroxyphenylalanine (termed "dopa"), oxidation and condensation occur with the formation of a dark brown or black pigment (*dopamelanin*) at certain definite places owing to the action of an intracellular oxidising enzyme, *dopaoxydase*. The oxydase is present in the protoplasm (not the nucleii) of the basal cells of the epidermis and the cells of the hair follicles, and is of a highly specific nature, exerting no action on tyrosine, quinol, homogentisic acid, pyrogallol, tryptophan, adrenaline, and other substances more or less closely related to 3:4-dihydroxyphenylalanine. A parallelism is observed between the pigmentary changes occurring in sections of skin under the action of chemically active light rays and those immersed in "dopa," and the conclusion is drawn that the natural pigment is probably formed in the living organism from 3:4-dihydroxyphenylalanine or a substance very similar to it in chemical constitution.

Dopaoxydase is destroyed on heating to 100°. Water, physiological salt solution, half-saturated ammonium sulphate solution, alcohol, acids, and alkalis also inactivate the enzyme; fat solvents, such as ether and benzene, do not destroy its activity. Poisons, such as prussic acid, toluene, formaldehyde, etc., also destroy the enzyme.

The action of dopaoxydase was tested, with negative results, on the following new substances. *α-Amino-β-4-hydroxy-3-methoxyphenylpropionic acid*, $C_{10}H_{13}O_4N$, is prepared by condensation of vanillin with hippuric acid, reduction of the resulting α-benzoylamino-β-4-hydroxy-3-methoxycinnamic acid, and subsequent elimination of the benzoyl radicle by heating with hydrochloric acid under a reflux condenser. The substance goes brown at 240° and melts at 256° (decomp.). It yields a momentary blue colour with a drop of ferric chloride, which then turns green and finally becomes colourless. *α-Amino-4-hydroxy-3-methoxyphenylacetic acid*, $C_9H_{11}O_4N$, is obtained by shaking vanillin in ethereal solution with potassium cyanide solution in the presence of ammonium chloride and proceeding in a manner similar to that described by Fromberg and Hermanns (A., 1914, i, 905) for the preparation of α-amino-4-hydroxyphenylacetic acid. It crystallises in white, silky needles, m. p. 240° (decomp.), and gives a momentary, olive-green colour with a drop of ferric chloride solution. On treatment with hydriodic acid the substance yields *α-amino-β-3:4-dihydroxyphenylacetic acid*, $C_8H_9O_4N$, white, crystalline powder, which gives a dark green colour with ferric chloride solution, turning intense purplish-red on the addition of sodium hydroxide. H. W. B.

Production of Creatinuria in Normal Adults. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1917, **31**, 561—566. Compare Denis, Kramer, and Minot, this vol., i, 526).—Feeding two normal women with a high protein (creatine-free) diet causes creatinuria, which disappears when the amount of protein in the diet is reduced. Similar experiments on two men invariably yielded negative results, although the amount of protein consumed was sufficient to raise the nitrogen eliminated in the urine to 34·5 grams daily. H. W. B.

Formation of Thiocyanic Acid in Animals. SERAFINO DEZANI (*Arch. Farm. sperim.*, 1917, **23**, 245—256; from *Chem. Zentr.*, 1917, ii, 178).—The decomposition of the nitriles of fatty acids in the animal organism occurs, according to Lang (*Arch. exp. Path. Pharm.*, **36**, 75), in such a manner that the cyano-group is eliminated and converted into thiocyanic acid, and the residue is completely oxidised; four-fifths to five-sixths of the acid is destroyed, whilst one-sixth to one-fifth appears in the urine. The hypothesis has been the subject of some criticism. The author has therefore estimated the ratio of acid sulphur to neutral sulphur in the urine of dogs to which acetonitrile had been administered. If Lang's hypothesis is correct, an increase in neutral sulphur, but also a much greater increase in acid sulphur, is to be expected, and consequently an increase in the above ratio. The amount of thiocyanic acid in the urine was smaller than that indicated by Lang and did not exceed one-tenth of that theoretically derivable from the administered nitrile. The presence of acetic acid in the urine could not be detected. With large and small doses of nitrile (in quantity insufficient to produce poisoning), the ratio of the two forms of sulphur diminished. With big doses, the total sulphur was decreased, the acid sulphur greatly increased, and the neutral sulphur almost unchanged. With small doses, the total sulphur was slightly increased, the effect being due to increase in the neutral sulphur. The author is therefore drawn to the conclusion that all the thiocyanic acid formed appears as such in the urine, and that the decomposition of the nitrile only occurs to a small extent in this sense; the greater bulk is probably hydrolysed and the acetic acid produced is completely oxidised in the organism.

The formation of thiocyanic acid after administration of nitriles has previously been observed only with mammals; the author finds it also to take place with fowls, but only in small quantity and after administration of large doses of nitriles. The greater resistance of birds to nitriles is confirmed. H. W.

Inhibition of Enzymic Reactions by Urine. HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1917, **100**, 202—225). —Normal and pathological urines contain a substance which strongly inhibits the enzyme action of invertase, catalase, and diastase. The substance is not destroyed by boiling the urine and is not adsorbed by animal charcoal. It does not appear to be urea or uric acid, neither is it a substance derived from the bile, because

it is insoluble in chloroform, and extracts of gall-stones do not exert any similar inhibitory action on the enzymes studied. The substance does not readily dialyse through parchment, which suggests that it is of colloidal nature in spite of its behaviour towards animal charcoal and heat.

The inhibitory substance occurs in very variable amounts in pathological as well as in healthy urines, and doubtless influences the actions of the enzymes which may be present. In diabetes, for instance, the low diastatic power of the urine (compare Wohlgemuth, A., 1909, ii, 1037) may be due either to a small amount of enzyme or to a large proportion of inhibitory substance accompanying a normal quantity of enzyme. H. W. B.

Toxicity of Phosphates in Relation to the Calcium in the Blood and to Tetanus. CARL BINGER (*J. Pharm. Exper. Ther.*, 1917, **10**, 105—120).—Solutions of phosphoric acid and its sodium salts, when injected intravenously into dogs, cause a diminution in the amount of calcium in the serum proportionate to the amount of phosphate introduced. When a dihydrogen phosphate is injected in an amount equivalent to 150 mg. of phosphorus per kilo. of body-weight, the calcium in the serum becomes reduced from 10 mg. to approximately 6 mg. per 100 c.c. of serum. After the injection of a di- or tri-alkali phosphate, a similar reduction in the calcium content of the serum is observed, but it is accompanied by typical symptoms of tetanus. The mechanism of the production of tetanus in these circumstances has not been elucidated (compare Greenwald, A., 1915, i, 1037). H. W. B.

Origin of Creatine. II. L. BAUMANN and H. M. HINES (*J. Biol. Chem.*, 1917, **31**, 549—559).—Incubation of minced animal tissues with glycocyamine does not lead to the production of creatine, but after the injection of glycocyamine into rabbits and dogs, an increased excretion of creatine is sometimes observed. The formation of creatine in the animal organism from arginine may therefore occur, with the intermediate formation of glycocyamine (compare Mellanby, A., 1908, ii, 308). H. W. B.

Comparative Investigation of the Behaviour of Hydroaromatic Substances in the Animal Organism. Y. SASAKI (*Acta Schol. Med. Kyoto*, 1917, **1**, 413—423; from *Physiol. Abstr.*, 1917, **2**, 344).—*Cyclo*hexanol and 1:4-dihydroxy*cyclo*hexane given by the mouth to rabbits, caused an increased output of ethereal sulphates and the appearance of glycuronic acid in the urine. Phloroglucinol, and *i*-inositol (*cyclo*hexane derivatives with three and with six hydroxyl groups respectively) did not do this, except that a single very large dose of phloroglucinol increased the output of ethereal sulphates in the dog. Toxicity tests on mice show that an increase in the number of hydroxyl groups decreases the toxicity. These substances are, in their biological behaviour, a link between the aliphatic alcohols and the aromatic phenols. G. B.

Toxic Action of Opium Alkaloids Individually and in Combination with each other on Paramœcia. DAVID I. MACHT and HOMER G. FISHER (*J. Pharm. Exper. Ther.*, 1917, **10**, 95—104).—Members of the papaverine group of alkaloids are very toxic towards *Paramœcium putrinum*, whereas members of the morphine group are comparatively innocuous. The toxic effect of a combination of two or more members of the same group of alkaloids is the sum of the toxic effects produced by each alkaloid separately. Combinations of members of different groups produce a synergistic effect, that is, the resultant effect is greater than the sum of the individual toxicities. It is probable that the toxicity of papaverine and other related alkaloids is associated with the benzyl group present in the molecule.

Papaverine, dionine, and, to a lesser degree, narcotine and narceine, exert a narcotic or anæsthetic action on paramœcia which is distinct from the toxic action. H. W. B.

Intermediate Metabolism in Experimental Phosphorus Poisoning. S. ISAAC (*Zeitsch. physiol. Chem.*, 1917, **100**, 1—33. Compare Frank and Isaac, A., 1911, ii, 315).—Perfusion experiments with the livers of dogs taken in the later stages of phosphorus poisoning show that under these conditions the normal transformation of lactic acid into dextrose and glycogen does not occur (compare Parnas and Baer, A., 1912, ii, 778). The primary degradation of saturated to unsaturated fats also appears to be inhibited, although the subsequent oxidation of the lower fatty acids occurs as in the normal animal. Phosphorus poisoning is not accompanied by any sign of lessened oxidation in the liver (compare Isaac and Loeb, following abstract). H. W. B.

Respiratory Metabolism of the Artificially Perfused Livers from Dogs after Phosphorus Poisoning. S. ISAAC and A. LOEB (*Zeitsch. physiol. Chem.*, 1917, **100**, 54—58).—In severe cases of phosphorus poisoning, the oxygen consumption per kilogram of liver tissue per minute during perfusion was found to fall within the limits obtained for livers from normal animals. Phosphorus poisoning is not accompanied, therefore, by diminished oxidative processes in the liver (compare Isaac, preceding abstract). H. W. B.

Volatility of Organic Compounds as an Index of the Toxicity of their Vapours to Insects. WILLIAM MOORE (*J. Agric. Research*, 1917, **10**, 365—371).—The work done on the benzene derivatives (compare this vol., i, 527) has been extended to a large series of other compounds, those studied being hydrocarbons, esters, acids, ethers, aldehydes, ketones, alcohols, haloid and thio-derivatives, nitro-compounds, nitriles, alkaloids, pyridine, and terpenes. In general, decreasing volatility is accompanied by an increase in toxicity. Compounds with boiling points of 225—250° and upwards are usually so slightly volatile that they

do not produce death in the case of the house-fly except after very long exposures. The author suggests that the structure of the respiratory system of the insect is probably responsible for the influence of volatility on the toxicity of the vapour of organic compounds.
W. G.

Chemistry of Vegetable Physiology and Agriculture.

Asymmetric Hydrolysis of Racemic Polypeptides by Killed Bacteria. I. T. Mito (*Acta Schol. Med., Kyoto*, 1917, **1**, 433—438; from *Physiol. Abstr.*, 1917, **2**, 320).—The bacterial ferments of *B. coli communis* and *Staphylococcus aureus* split *dl*-leucylglycine asymmetrically; this peptide resists pancreatic ferments. The copper salt of *l*-leucine was isolated, whilst the optical activity of the mother liquor was compatible with the presence of *d*-leucylglycine. G. B.

Asymmetric Splitting of Racemic Tyrosine by Bacillus proteus vulgaris and Bacillus subtilis (Biological Method of Preparing *d*-Tyrosine). M. Tsudji (*Acta Schol. Med., Kyoto*, 1917, **1**, 439—448; from *Physiol. Abstr.*, 1917, **2**, 320).—With the former organism 65—76% of *d*-tyrosine was isolated and identified; *d*-*p*-hydroxyphenyl-lactic acid, *p*-hydroxyphenylpropionic acid, and *p*-hydroxyphenylethylamine were isolated from the decomposition products, and were derived from *l*-tyrosine. The author claims that *B. proteus* is a suitable agent for the preparation of *d*-tyrosine. With *B. subtilis* there was only a very slight degree of cleavage. G. B.

Chemical Composition and Formation of Enzymes. XIII. Alterations in the Amount of Enzyme in Kephir Cells and in B. lactis acidi. H. Euler [with E. Griese] (*Zeitsch. physiol. Chem.*, 1917, **100**, 59—68. Compare Euler and Cramér, A., 1914, i, 364).—Kephir cells which have been grown previously once or twice in a mixture of whey and galactose, with and without the addition of phosphates, contain a larger quantity of enzyme in relation to dry weight than is contained in the original material. In other words, the same weight of kephir cells produces a more rapid and a greater evolution of carbon dioxide after propagation in a suitable medium than in the original condition.

When the lactic acid bacillus is similarly grown in successive fresh quantities of a medium of whey containing 4% of galactose, the rate of formation of lactic acid by a standard number of bacilli is increased. If, however, 6% of sodium dihydrogen or disodium hydrogen phosphate is also present in the medium, the formation of the lactic acid soon diminishes, and, instead, an increasing quantity

of carbon dioxide is produced. By suitable preliminary treatment, therefore, it is possible to stimulate the production of one or other of the enzymes in the living cell. H. W. B.

Biochemical Activity of Agglutinated Bacteria. AMILCARE ZIRONI (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 19—23).—The author's experiments on the paratyphoid bacillus *B* and the cholera vibrio show that these organisms produce the same quantity of acid and of carbon dioxide, and reduce methylene-blue to the same extent respectively, whether they are agglutinated or not.

R. V. S.

Glycolysis. GERSON G. WILENKO (*Zeitsch. physiol. Chem.*, 1917, **100**, 255—263).—The fermentation of dextrose by yeast occurs without the formation of carbon dioxide when the hydroxyl-ion concentration of the medium is maintained within certain limits. This can be effected by adding a buffer-mixture of sodium dihydrogen and disodium hydrogen phosphates in the proportion of one of the former to ten or more (depending on the kind of yeast) of the latter. The same result can be achieved without phosphates by the simple addition of a slight excess of *N*-sodium hydroxide solution. If the yeast at the end of an experiment is collected and treated with fresh dextrose solution, ordinary fermentation with evolution of carbon dioxide ensues, indicating that in the original experiment the hydroxyl ions are associated with the dextrose or its degradation products rather than directly with the enzyme. H. W. B.

Alcoholic Fermentation at Different Concentrations of Hydroxyl Ion. HANS EULER [with KNUT HALDIN] (*Zeitsch. physiol. Chem.*, 1917, **100**, 69—73. Compare Wilenko, preceding abstract).—The fermentation of dextrose by yeast proceeds even in the presence of alkalinity equivalent to *N*/20-ammonium hydroxide solution. If an adequate proportion of ammonium phosphate is also added, the production of carbon dioxide is greatly diminished, although the amount of dextrose fermented may be as great as it was before the addition of the ammonium phosphate, similar conditions of time, temperature, and concentration being maintained.

H. W. B.

The Increase of Dry Weight of Yeast when Urea is Used as the Source of Nitrogen. TH. BOKORNY (*Biochem. Zeitsch.*, 1917, **82**, 359—390).—A number of experiments are quoted which show that considerable growth of yeast (as measured by increase in dried weight) can take place when the organism is grown on urine containing sugar. The urea, and not hippuric acid, acts as the source of nitrogen. The growth is especially vigorous in presence of air. S. B. S.

Saccharophosphatase of Yeasts and the Fermentation of Sucrose Phosphoric Acid. KEMAL DJENAB and CARL NEUBERG (*Biochem. Zeitsch.*, 1917, **82**, 391—411).—Yeasts contain a ferment

"saccharophosphatase," which can hydrolyse the salts of synthetic sucrose phosphoric acids, prepared originally by Neuberg and Pollak (hesperonal). Scission of inorganic phosphate takes place. The ferment is found both in top and bottom yeasts. It is to be distinguished from the already known hexophosphatase in that the latter acts only in yeast juices separated from the living cell, whereas the new saccharophosphatase will act in the living cell, and produce alcoholic fermentation of the synthetic sucrose phosphate. It is also insensitive to the action of antiseptics, both when fresh yeast is used or maceration juice. It acts between the temperatures of 22° and 37°, and in neutral, alkaline, and weakly acid (acetic acid) solutions. The soluble sodium salts of the synthetic sucrose phosphoric acid can be hydrolysed to the extent of 67% by fresh yeast and 45% by maceration juice. S. B. S.

Autoregulation of the Course of Reaction in Fermentative Processes. L. Lichtwitz (*Deut. med. Woch.*, 1917, **43**, 643—646; from *Chem. Zentr.*, 1917, ii, 106).—Enzymatic processes in closed system lead to a true equilibrium or to a cessation of action, the latter state being caused by inactivation of the ferment. Natural systems of reaction are not closed, since the ultimate products are continuously removed either by subsequent processes or by separation. In natural systems, a chain of processes is always involved, in which a fixed order of velocities of reaction is always maintained (for example, the intermediate storage of sugar). This order is caused by the action of the products of fermentation on the ferment itself. The mechanism of such action is explained by an investigation of the kinetics of the inversion and fermentation of yeast. The application of these ideas is extended by investigations of the final stages of the decomposition of albumin and by consideration of protein metabolism. H. W.

Behaviour of some Organic Substances in Plants. VIII. G. Ciamician and C. Ravenna (*Gazzetta*, 1917, **47**, ii, 99—107).—The experiments were conducted by watering seeds, and subsequently the growing plants. with 1% solutions of the substances investigated. In the case of maize and beans, evidence of the production of salicin was obtained when saligenin was administered. When beans are treated in the same way with benzyl alcohol, traces of a compound are formed, which yields the alcohol again when boiled with hydrochloric acid. In the same way, quinol gives rise to a compound, probably of the nature of a glucoside. R. V. S.

Relationship between Sugar Fermentation and Sugar-Assimilation. Th. Bokorny (*Allg. Brau- Hopfen-zeitung*, 1917, **57**, 447—480; from *Chem. Zentr.*, 1917, ii, 23).—External factors have, without doubt, a considerable influence on this relationship. Light, which is necessary with green plants, is probably unimportant with respect to yeast, but access of air has a more marked effect. In the present communication, the influence of fractional addition of sugar, of nitrogen nutriment, and of addition of alkali

are considered. The increase in dry substance in the fermenting yeast is regarded as a criterion of the extent of assimilation. Under unfavourable conditions a loss in weight occurs, but, in better circumstances, the extent of assimilation exceeds that recorded by Pasteur, according to whom about 1% of the sugar is assimilated. Repeated addition of sugar without alteration in the total quantity appears beneficial. Carbamide, even in pure aqueous solution, is a more suitable source of nitrogen than ammonia; apparently this is more effective when gradually formed than when applied in the preformed state. Similarly, assimilation is favoured by the substitution of sucrose for dextrose. Assimilation is promoted by free potassium hydroxide at certain concentrations, preferably at about 0·01%. Previous experiments on the application of dextrose as a food for moulds and for the formation of starch in Spirogyræ are discussed; in the latter instance, the influence of light and of access of oxygen is particularly noticeable. H. W.

Benzene Derivatives as Sources of Nourishment. TH. BOKORNY (*Zentr. Physiol.*, 1917, **32**, 55—63; from *Chem. Zentr.*, 1917, ii, 22).—It has been observed that the cells of certain plants (fungi, moulds, algæ) are capable of utilising derivatives of benzene for the production of albumin. Since it has been shown by Loew that quinic acid, which is frequently present in the cells of plants, can be decomposed into two molecules of propionic acid, and that the latter can be assimilated, the author puts forward the hypothesis that quinic acid is first produced in the cell from assimilable benzene derivatives and is subsequently decomposed into propionic acid and carbon dioxide. H. W.

The Physiological Significance of Potassium in Plants. JULIUS STOKLASA (*Biochem. Zeitsch.*, 1917, **82**, 310—323).—The author replies in detail to the criticisms of Weevers (this vol., i, 372).—The latter maintains that potassium is essential to the synthesis of proteins in plants, whereas the former maintains that it is essential for synthesis of carbohydrates. A large number of results already published are quoted which are stated to support the thesis of the author. S. B. S.

A New Reagent for Phloroglucinol and Catechol: the Distribution of these Substances in the Plant Kingdom. MARIANNE JOACHIMOWITZ (*Biochem. Zeitsch.*, 1917, **82**, 324—358).—*p*-Dimethylaminobenzaldehyde dissolved in sulphuric acid is a reagent for phloroglucinol, and gives a quicker and more localised reaction than Lindt's reagent. It was applied (microchemically) to the investigation of 464 different plants to determine the distribution of substances giving a coloration with it. Catechol gives the same reaction with this reagent, and macrochemical investigation reveals the fact that in many cases the coloration produced is due, at any rate partly, to this substance. S. B. S.

Wasahba Wood. G. BURTON BAKER (*Chem. News*, 1917, **116**, 139).—Wasahba wood is a very hard, almost bony wood, D 1·214,

which is sometimes used for fishing rods. The tree is supposed to be a native of British Guiana, where it attains a diameter of about 3 ft. When under the plane, the wood produces a quantity of resinous, gamboge-like dust which becomes salmon-pink with soap or alkalis. An alcoholic extract is colourless, and may be used as an indicator in the titration of ammonia and alkali hydroxides, the readings being almost the same as those obtained with phenolphthalein. An alkaline extract is a good stain for white wood.

J. C. W.

Presence of Nitrites and Ammonia in Diseased Plants. II. Oxydases and Diastases; their Relation to the Disturbance. P. A. Boncquet and Mary Boncquet (*J. Amer. Chem. Soc.*, 1917, **39**, 2088—2093. Compare this vol., i, 74).—The phenomena in some plants infected by nitrate-reducing organisms seem to be co-ordinated for the preservation and increase of the nitrogen content of the plant tissues. The oxidising enzymes present appear to assist this purpose by tending to neutralise the reducing activities of the invading bacteria; the reduction in the size of secondary organs seems intended to economise the nitrogen and to preserve it for the more essential parts, such as the roots and leaves; the increased transpiration of water and the increase in the root system also are indicative of an augmented tendency to supply the plant with the necessary nitrates. The higher percentage of ash in diseased plants of this type is probably the result of these endeavours, but the fact that nevertheless a deficiency of total nitrogen is found in the tissues suggests that the reducing bacteria, in converting the nitrates into nitrites and ammonia, cause a waste of this element and induce a disease of nitrogen starvation.

D. F. T.

Symptoms of Poisoning by certain Elements, in Pelargonium and other Plants. E. E. Free (*The Johns Hopkins Univ. Circular*, 1917, 195—198 [393—396]; from *Physiol. Abstr.*, 1917, **2**, 389).—Compounds of As, Ba, Br, Co, Cu, Pb, Mn, Ni, Ag, Ur, V, and Zn gave no determinable poisonous effects in the concentrations used. Pronounced toxic effects of B, Cr, I, Li, and Hg on the leaves are described. The evidence suggests that the poisons caused injury where the transpiration of water increased the concentration of the poison locally.

G. B.

The Occurrence and Significance of Mannitol in Silage. Arthur W. Dox and G. P. Plaisance (*J. Amer. Chem. Soc.*, 1917, **39**, 2078—2087).—In the production of maize silage, the amount of volatile acid, lactic acid, carbon dioxide, and alcohol formed is insufficient to account for the whole of the sucrose which has undergone fermentation, and the deficit is largely explained by the formation of mannitol which originates from the fructose portion of the sucrose molecule by bacterial reduction. During the fermentation of silage, the quantity of mannitol present gradu-

ally increases until approximately the twelfth day, after which a rapid decrease sets in, probably due to further bacterial alteration. The suggestion is made that mannitol could be economically extracted from silage and converted on a commercial scale into the nitrate for use as an explosive. D. F. T.

Methods for Determining the Reaction of Soils. HARALD R. CHRISTENSEN (*Soil Sci.*, 1917, **4**, 115—178).—A review is given of the various methods which have been proposed for the determination of the acidity and the lime requirement of the soil. On the basis of a considerable number of comparative experiments with Danish soils, the author suggests the necessity of distinguishing between the absolute acidity of the soil and its ability to liberate acids from neutral salt solutions (that is, to absorb bases). This distinction is, however, somewhat arbitrary, as for the former purpose the use of potassium chloride solutions is mentioned, whilst for the latter, solutions of calcium acetate are considered suitable.

These two methods were employed extensively, and the results of the tests correlated with the behaviour of the soil towards the acid test for free carbonate, the litmus, potassium iodide–iodate, and *Azotobacter* tests. The use of *p*-nitrophenol as a soil acidity indicator was also adopted.

In general, the digestion of soils with calcium acetate solution gave high positive results, even in the case of neutral and slightly alkaline soils, whilst greater correspondence was shown between the potassium chloride and the various qualitative methods. With distinctly acid soils, the ratio between the amount of acid liberated in potassium chloride and calcium acetate solutions was often below 1 : 10, but with neutral and slightly acid soils it frequently rose to 1 : 40 or more.

It is considered that in some soils part at least of the reaction is due to the presence of truly acid substances, and this agrees with the results of electrometric determinations.

A determination of the base absorption power of a soil (calcium acetate method) is not sufficient for indicating its lime requirement, nor do the results of the acidity method (with potassium chloride) give positive information on the point. It is stated, however, that all mineral soils having an acid reaction for litmus have a large lime requirement, but that many soils neutral to litmus also respond to treatment.

The lime requirement of a soil appears to be determined by the presence or absence of certain easily decomposable calcium (or magnesium) compounds capable of neutralising acids, but the question remains open as to which method will serve to indicate this need. H. B. H.

Organic Chemistry.

Condensation of Unsaturated Systems. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 932—939).—A theoretical paper, in which the author discusses the condensation of unsaturated compounds in the light of his theory of valency and affinity. A. J. W.

The Supposed Keto-enol Isomerism of Ethyl Succinylsuccinate and Ethyl *p*-Dihydroxyterephthalate. A. HANTZSCH (*Ber.*, 1917, **50**, 1213—1216. Compare Gibbs and Brill, A., 1915, i, 648, and Brill, A., 1916, ii, 591).—It is claimed that Brill's evidence that the above esters exist, even in the state of solids with constant m. p.'s, as keto-enol mixtures, is based on wrong results obtained in the Meyer titration for enols (compare Hantzsch's views, A., 1915, i, 495, 551). J. C. W.

Bile Acids. III. Structural Relations between Cholic and Deoxycholic Acids. HEINRICH WIELAND and HERMANN SORGE (*Zeitsch. physiol. Chem.*, 1916, **98**, 59—64).—On distillation of deoxycholic acid in a vacuum (12 mm.) at 320—340°, a heavy oil distils over and solidifies to a colourless resin, which consists of *β-choladienecarboxylic acid*, $C_{24}H_{36}O_2$. It crystallises in slender needles which, when heated, soften at 127°, m. p. 132—133°. It gives a coloration with acetic anhydride and sulphuric acid which is first red, then brown, and finally olive-green; at the same time, an intense green fluorescence is exhibited, which is also produced by the sulphuric acid alone. The substance is unsaturated and decolorises permanganate solution; it is isomeric with the choladienecarboxylic acid obtained by the reduction of cholatrienecarboxylic acid, which has been prepared by the distillation of cholic acid (Wieland and Weil, A., 1912, i, 830). Further reduction by hydrogen in the presence of palladium black converts both *α*- and *β*-choladienecarboxylic acids into the same cholanecarboxylic acid. It follows, therefore, that deoxycholic acid differs from cholic acid in having only two instead of three alcoholic hydroxyl radicles, so that these compounds may be termed the dihydroxy- and the trihydroxy-cholanecarboxylic acids respectively.

It has been shown (Wieland and Weil, *loc. cit.*) that on oxidation of cholatrienecarboxylic acid with permanganate a molecule of acetic acid is formed, which indicates the presence of a $C\colon CH\cdot CH_3$ group. Cholic acid itself therefore probably contains the grouping $C(OH)\cdot CH_2\cdot CH_3$ or $CH\cdot CH(OH)\cdot CH_3$. It is now shown that *β*-choladienecarboxylic acid when similarly oxidised with permanganate does not yield any acetic acid. It follows that the above hydroxyl radicle is absent in deoxycholic acid, whilst probably the remaining hydroxyl radicles occupy the same positions in each acid.

When the distillation of deoxycholic acid is carried out rapidly, a

compound is obtained which is isomeric with β-choladienecarboxylic acid. It crystallises in needles, which, when heated, soften at 204°, m. p. 215—217°. The new substance is not an acid, and does not give a Liebermann colour reaction. H. W. B.

Osazones from Mixtures of Formaldehyde and Starch. H. MAGGI and G. WOKER (*Ber.*, 1917, **50**, 1188—1189. Compare this vol., i, 61, 447).—An osazone, m. p. 181—182°, crystallising in yellow rosettes, has been obtained from the dialysate of a mixture of formaldehyde and starch which had been kept at 40—50° for half-an-hour. The sugar may possibly be a mixture of maltose and *iso*maltose. It is fermentable by yeast. J. C. W.

Formaldehyde as a Hydrogenase Model, and some Observations on Formaldehyde Condensations. G. WOKER and H. MAGGI (*Ber.*, 1917, **50**, 1189—1191).—Solutions of lead acetate containing formaldehyde and sulphur soon darken at 100°, and appear distinctly dark if left in the light for some days at the ordinary temperature, owing to hydrogenation of the sulphur. Lead acetate is much more soluble in "formalin" than in water. The hot solution keeps its colour for a long time, but slowly develops the odour and tint of caramel. Apparently, the increased solubility of the lead salt is due to the union of the aldehyde with the metal, which then induces the polymerisation to formose. It is suggested that a similar attachment of formaldehyde to magnesium in the chlorophyll may precede the production of formose in green plants. J. C. W.

Preparation of Aldol. N. GRÜNSTEIN (U.S. Pat., 1234156 and Brit Pat., 101636; from *J. Soc. Chem. Ind.*, 1917, **36**, 1064).—Acetaldehyde, mixed with a little water, is treated with the oxide of an alkaline earth metal, such as strontium oxide. The resulting solution is neutralised with acid and distilled in a vacuum. Alkaline-earth carbides may be added to serve as catalysts, and the reaction may be started with only part of the acetaldehyde, the remainder being added as the reaction proceeds. H. W.

Reduction of Aliphatic Nitrites to Amines. PANCHĀNAN NEOGI and TARINI CHARAN CHOWDHURI (T., 1917, **111**, 899—902).—Gaudion (A., 1912, i, 163) has described the reduction of aliphatic nitrites to mixtures of primary, secondary, and tertiary amines by hydrogen in the presence of finely divided nickel at 220—230°. If nickelised asbestos is used, the reduction proceeds readily at 125—130°, and the primary amine alone is produced. This temperature is favourable to the conversion of the nitrite into the nitroparaffin (compare A., 1916, i, 626). J. C. W.

Transformation of Secondary and Tertiary Aliphatic Amines into Nitriles. ALPH. MAILHE and F. DE GODON (*Compt. rend.*, 1917, **165**, 557—559).—When the vapour of di*iso*amylamine is passed over nickel at 320—330° it is decomposed, the products

being hydrogen, an unsaturated hydrocarbon, some tri*iso*amylamine, and some *iso*valeronitrile. When the vapour of tri*iso*amylamine is passed over nickel at 360—370° it yields hydrogen, an unsaturated hydrocarbon, and some *iso*valeronitrile. W. G.

Methyleneamino-acids. HARTWIG FRANZEN and ERNST FELLMER (*J. pr. Chem.*, 1917, [ii], **95**, 299—311).—In only a few cases can methyleneamino-acids be prepared by evaporating solutions of the acids with formaldehyde, or by adding alcohol to concentrated solutions of the acids mixed with formaldehyde. The salts, however, are comparatively stable in cold water, and can be obtained by evaporation. They are mostly freely soluble, but some can be prepared as precipitates by double decomposition between a very soluble salt and a suitable compound of the other metal. The action of boiling water on the compounds is being investigated.

Methyleneaminoacetic acid yields a *barium* salt, $4H_2O$, a *calcium* salt, $4H_2O$, and a bluish-violet *copper* salt, $2H_2O$. *Methyleneglycylglycine*, $CH_2{:}N{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,2H_2O$, a hygroscopic powder, forms a *barium* salt, $4H_2O$. α-Methyleneaminopropionic acid gives a *barium* salt, $4H_2O$, a *calcium* salt, $2H_2O$, and a *copper* salt, $2H_2O$. *β-Methyleneaminopropionic acid*,

$$CH_2{:}N{\cdot}C_2H_4{\cdot}CO_2H,H_2O,$$

yields *calcium* and *barium* salts, both with $2H_2O$. *Methylenephenylalanine* and its *copper* salt crystallise with $2H_2O$, the *barium* salt with $1H_2O$. Methyleneasparagine gives a *barium* salt, $3H_2O$, and a *calcium* salt, $4H_2O$. J. C. W.

Desulphurisation of Thiocarbamides (Formation of Carbamide). ERNST SCHMIDT (*Arch. Pharm.*, 1917, **255**, 338—351).—Whilst ψ-thiohydantoin yields guanidine and oxalic acid when heated with mercuric oxide in concentrated aqueous ammonia, lead ψ-thiohydantoin heated with aqueous ammonia in a sealed tube at 115—120° yields, in addition to lead sulphide, acetic acid, and other substances, carbamide in considerable quantity. This formation of carbamide is all the more astonishing because Hofmann in his classical researches on the desulphurisation of thiocarbamides states that not a trace of carbamide is formed when thiocarbamide is desulphurised.

Employing xanthydrol, which Fosse has shown will detect carbamide in a dilution of one part in a million, as the reagent, the author now shows that carbamide is produced, although only in very small quantity, when thiocarbamide in aqueous solution containing a little ammonium thiocyanate is desulphurised by mercuric oxide. Whether the carbamide is formed directly from the thiocarbamide by the replacement of the sulphur atom by an oxygen atom or by a secondary reaction from the cyanamide, which is also produced by the desulphurisation, cannot be stated, because a solution of cyanamide under the same conditions also gives a precipitate of xanthydrol–carbamide.

Dicyanodiamide, guanidine, creatine, and creatinine do not yield

precipitates with xanthydrol, but thiocarbamide, hydantoin, and thiohydantoin do.

Carbamide is also formed, probably at the expense of the cyanamide, when thiocarbamide is desulphurised by silver nitrate or lead acetate in aqueous ammonia. C. S.

Formation of Carbamide from Cyanamide. ERNST SCHMIDT (*Arch. Pharm.*, 1917, **255**, 351—357. Compare preceding abstract).—A solution of cyanamide in moist ether, after being kept for fourteen days at the ordinary temperature, deposits crystals consisting of a mixture of carbamide and dicyanodiamide; the former is best isolated by treating a glacial acetic acid solution of the mixture with a freshly prepared 3—5% solution of xanthydrol in glacial acetic acid; the quantity of the crystalline xanthydrol–carbamide compound obtained is very small, 10 grams of cyanamide yielding only 0·35 gram.

When cyanamide is repeatedly evaporated to dryness with water, carbamide is formed in slightly greater quantity, 10 grams of cyanamide yielding 0·68 gram of the xanthydrol compound. A yet larger amount of carbamide is formed when cyanamide is repeatedly evaporated to dryness with a solution of hydrogen peroxide. When a solution of cyanamide in moist ether is treated with an ethereal solution of oxalic acid, a precipitate of carbamide oxalate is rapidly obtained. C. S.

The Prussian Blue Hydrosol. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1917, **100**, 77—94).—The green solutions obtained by adding a large excess of potassium ferrocyanide to ferric chloride do not contain a definite green double salt or other compound. The addition of salts, alcohol, or hydrochloric acid precipitates the ordinary blue solid, and the same product is obtained even by the addition of a concentrated solution of potassium ferrocyanide. The same green shade may be obtained by adding a dilute solution of colloidal ferric hydroxide to a blue solution of ferric ferrocyanide.

Ultramicroscopical examination shows that the fineness of the particles of the hydrosol increases with increasing proportion of potassium ferrocyanide, and the change to blue on addition of salts is accompanied by increasing coarseness of particles. Either the residue obtained by ultra-filtration or a fresh precipitate of 'insoluble' Prussian blue may be brought into the state of a hydrosol by addition of potassium ferrocyanide. The particles are negatively charged in a solution containing an excess of potassium ferrocyanide, but positively charged in presence of an excess of ferric chloride. Analysis of the precipitate from a green solution shows the presence of ferric hydroxide. The colour is therefore a mixed colour, resulting from the blue of Prussian blue and the yellow of colloidal ferric hydroxide. C. H. D.

Semicarbazones of α-Ketonic Acids. Acylsemicarbazides and Acylsemicarbazic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], **21**, 180—190).—A more detailed account of work already

published (compare this vol., i, 417). The following semicarbazides are described. Phenylacetylsemicarbazide,

$$CH_2Ph\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 156°, giving a *hydrochloride*, m. p. 170°; *αα-dimethylpropionoylsemicarbazide*, $CMe_3\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 215°; *α-phenylcinnamoylsemicarbazide*,

$$CHPh{:}CPh\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 230°, giving a *hydrochloride*, m. p. 210°. All these semicarbazides are hydrolysed by dilute acids or alkalis, giving the free acid, hydrazine, carbon dioxide, and ammonia. They are oxidised by alkaline hypoiodites or hypobromites, giving the salt of the acid, the alkali cyanate, and nitrogen. W. G.

Coal Distillation under Pressure. J. H. CAPPS and G. A. HULETT (*J. Ind. Eng. Chem.*, 1917, **9**, 927—935).—In the distillation of coal, increase of pressure up to 20 atmospheres causes a decrease in the amounts of high boiling compounds and an increase in the amounts of low boiling compounds present in the vapours evolved below 600°; the quantity of low boiling aromatic substances in these oils is also increased. These results are due to "cracking" or thermal decomposition of the vapours of the heavy compounds. Increased pressure also, in many cases, reduces the quantities of phenols and acid substances in the distilled oils. Further, a larger amount of coke is obtained; the calorific value of the coke is increased, whilst the amounts of nitrogen, oxygen, sulphur, and volatile substances contained in it are decreased. The volume of gas evolved from coal below 600° is increased when the coal is distilled under pressure. W. P. S.

Preparation of Phenol [from Cresols]. H. TERRISSE (Brit. Pat., 108938; from *J. Soc. Chem. Ind.*, 1917, **36**, 1091).—A mixture of cresols is fused with a large excess of sodium or potassium hydroxide and treated with an oxidising agent, such as copper oxide or peroxide of lead, manganese, barium, iron, or the like, in order to convert the cresols into the corresponding hydroxybenzoic acids. The product may be treated in one of two methods: (1) The fused mass is cooled on iron plates, pulverised, and heated at about 300° in iron tubes through which a current of carbon dioxide is passed. The phenol is condensed in suitable receivers. (2) The free hydroxybenzoic acids are isolated, dried, and heated in a still with crude anthracene oil at about 250°, when carbon dioxide is liberated and phenol distils over. The second method is not so satisfactory as the first, owing to the large amount of acid required to neutralise the alkali hydroxide; also, in the first method, the residual alkali carbonate can be causticised and used again. H. W.

Solubility of Thymol in Mixtures of Water and Glycerol. M. MARQUINA (*Anal. Fis. Quim.*, 1917, **15**, 262—271).—At 25°, 100 parts of water dissolve 0·0952 part of thymol, and 100 parts of glycerol 1·71 parts of thymol. For mixtures of the two solvents, the solubility of thymol increases with the percentage of glycerol. A. J. W.

Polymerides of Methylchavicol. P. VAN ROMBURGH and J. M. VAN DER ZANDEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 64—65).—A further study of the polymerides of methylchavicol obtained by heating it in a sealed tube at 250° for forty-eight hours (compare A., 1909, i, 597). The compound, m. p. 166°, gives a *bromide*, m. p. 139°. The compound, m. p. 98°, when oxidised with potassium permanganate in acetone solution, gives, in addition to anisic acid, an *acid*, $C_{12}H_{16}O_3$, m. p. 113°, which on further oxidation gives a second *acid*, m. p. 138°. Oxidation of the compound, m. p. 166°, only yields anisic acid. *p*-Tolyl methyl ether has been isolated from the products produced by heating methylchavicol as described above. W. G.

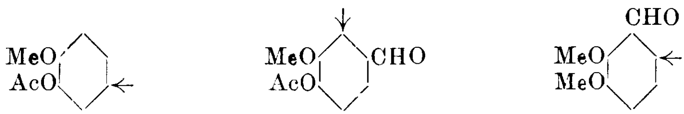
Synthesis of 4-Hydroxy-1-β-aminoethylnaphthalene [4-β-Aminoethyl-α-naphthol]. A. WINDAUS and DAISY BERNTHSEN-BUCHNER (*Ber.*, 1917, **50**, 1120—1123).—This base has been synthesised in order to compare its physiological activity with that of adrenaline and simple phenolic bases generally; unlike *p*-hydroxyphenylethylamine, the simplest prototype of adrenaline, it is only very slightly active.

4-Methoxy-α-naphthaldehyde is converted into the corresponding acrylic acid by Perkin's method (Rousset, A., 1899, i, 296), and this is reduced by means of hydrogen and colloidal palladium to β-4-*methoxy*-1-*naphthylpropionic acid*, which crystallises in glistening needles, m. p. 165—166°. The ethyl ester is converted into the *hydrazide*, bundles of needles, m. p. 155—156°, then into the azide, a yellow powder, and this is transformed into the urethane by boiling with alcohol, as usual. *Ethyl* β-4-*methoxy*-1-*naphthylethylcarbamate*, $OMe\cdot C_{10}H_6\cdot CH_2\cdot CH_2\cdot NH\cdot CO_2Et$, crystallises in white needles, m. p. 116—117°, and is hydrolysed by prolonged boiling with hydrochloric acid to the *hydrochloride* of β-4-*hydroxy*-1-*naphthylethylamine* (4-β-*aminoethyl*-α-*naphthol*), $C_{12}H_{13}ON,HCl$, glistening, quadratic leaflets, m. p. 239—240° (decomp.). The base forms a *dibenzoyl* derivative, m. p. 203—204°, and a *diacetyl* compound, m. p. 139—140°. J. C. W.

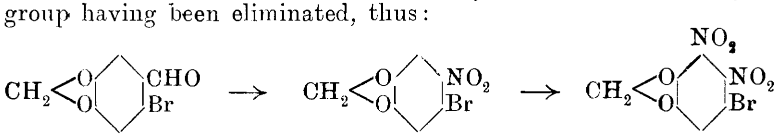
Experiments on the Orientation of Substituted Catechol Ethers. THOMAS GILBERT HENRY JONES and ROBERT ROBINSON (T., 1917, **111**, 903—929).—A number of observations on the orientation of members of the series of catechol ethers are recorded. Extensive references to earlier work by Robinson and others are supplemented by a number of new facts.

I. *Substitution in Catechol Dimethyl and Methylene Ethers, and their Derivatives.*—(*a*) Only mono-derivatives, substituted in position 4, are obtained by direct attack on the catechol ethers. (*b*) With only two authenticated exceptions, di-substitution gives rise to the 4:5-derivatives. (*c*) In the preparation of 3:4:5-derivatives from a 4:5-substituted catechol ether, the new substituent enters the ortho-position with regard to the more negative of the groups occupying positions 4 and 5, unless the more positive group is powerfully ortho-directive.

II. *Influence of a Negative Group on a Positive Group in the Meta-position.*—Substitution in a compound which contains a negative group in the meta-position with regard to a positive group takes place at the position between these two groups, unless it is already occupied by another positive group, when the new substituent enters the para-position; for example, whilst acetylguaiacol is nitrated in the para-position with respect to the methoxy-group, acetylvanillin is attacked between the methoxy- and aldehydo-groups, and veratraldehyde next to the aldehydo-group, thus:

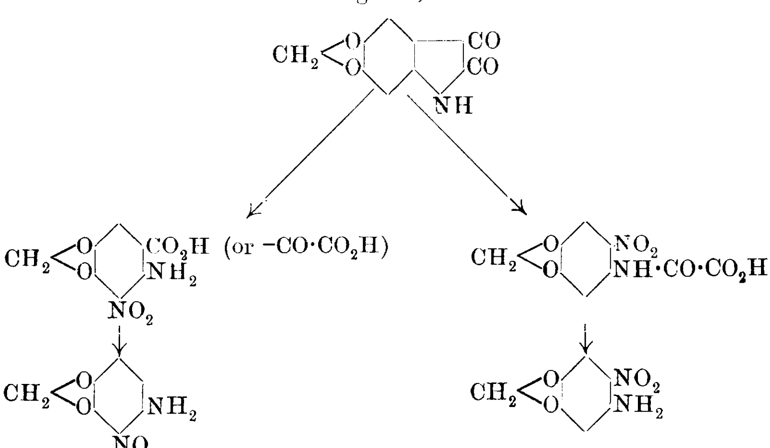


III. *Nitration of Bromopiperonaldehyde.*—Oelker (A., 1891, 1474) described a "bromonitropiperonaldehyde," m. p. 89°, and a "bromodinitropiperonaldehyde," m. p. 172°, as the products of the nitration of 6-bromopiperonaldehyde. These compounds are now shown to be nitrated bromocatechol methylene ethers, the aldehydo-group having been eliminated, thus:



The dinitro-compound loses bromine on reduction to the diamine, but the corresponding veratrole derivative retains its bromine and yields a bromodiaminoveratrole.

IV. *Action of Nitric Acid on Methylenedioxyisatin.*—When methylenedioxyisatin is oxidised by nitric acid, an acid is produced which loses carbon dioxide on treatment with sodium carbonate, yielding a nitroamine (Herz, A., 1905, i, 778). A correct interpretation of this reaction is now given, thus:

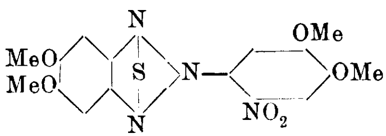


Herz. Robinson.

V. *A Reaction of Piperonylic Acid.*—When piperonylic acid in sodium carbonate solution, but not in acetic acid, is treated with bromine water, but not with sodium hypobromite, 4 : 5-dibromocatechol methylene ether is precipitated. This forms a pale yellow solution in sulphuric acid, which is changed to crimson on the addition of a trace of nitric acid.

In the above reaction, the carboxyl group is displaced by bromine and then the monobromo-derivative is further brominated. Similarly, 4 : 5-dimethoxy-*o*-toluic acid yields 6-bromohomoveratrole. Apparently, the reaction is fairly general and may help in the identification of acids derived from alkaloids and other natural products, as Perkin has already shown (T., 1916, **109**, 918).

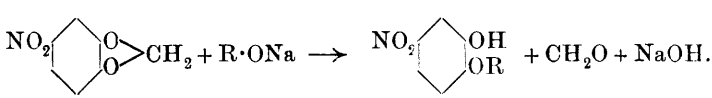
VI. *Phenanthraphenazine Derivatives.*—Many *o*-dinitro- and *o*-nitroamino-compounds have been characterised by reducing them to *o*-diamines and, without isolation, converting these by means of phenanthraquinone into phenanthraphenazines. The ethers of 1 : 2-dihydroxyphenanthraphenazine are bright yellow and exhibit green fluorescence in neutral solvents, whilst ethers of 2 : 3-dihydroxyphenanthraphenazine are pale yellow and give almost colourless solutions with intense violet fluorescence. This can be turned to practical account in deciding whether a plant product is a veratrole derivative substituted only in positions 4 or 4 and 5, positive results being obtained in many cases with as little as 0·05 gram of material.



VII. *A New Heterocyclic Nucleus.*—An unusual result is recorded in the reduction of 4 : 5-dinitroveratrole. An orange-yellow product is obtained of the formula $C_{16}H_{16}O_6N_4S$, which is best represented by the annexed formula. The SN_3-grouping is designated "thiotriazo."

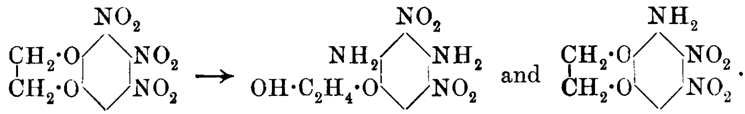
For experimental details, see original. J. C. W.

The Scission of certain Substituted Cyclic Catechol Ethers. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1917, **111**, 929—940).—When 4-nitrocatechol methylene ether is warmed with sodium methoxide or ethoxide solution, a 5-nitro-2-alkyloxyphenol is obtained, according to the scheme:



The corresponding ethylene ether, however, does not react in this way, but a scission of the ethylenedioxy-ring has been examined in the case of 4 : 5 : 6-trinitroethylenedioxybenzene. This reacts with ammonia to form two compounds, in one of which the ring has been opened by the addition of the elements of ammonia and the 5-nitro-group replaced by the amino-group, whilst in the other the nitro-

group in position 6 has been displaced by the amino-group, thus:

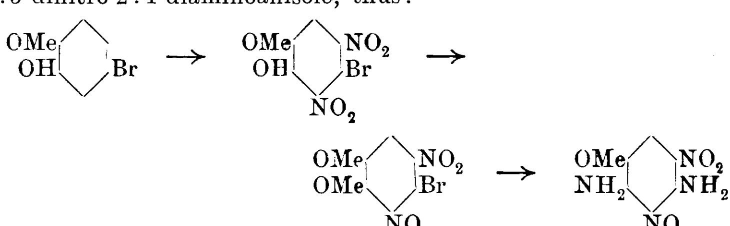


The constitution of the former compound is proved by its conversion, through simple stages, into the known 3:5-dinitro-2:4-diaminoanisole, and that of the latter by the production from it of 4:5-dinitroethylenedioxybenzene. The weak attachment of the 6-nitro-group in the trinitroethylenedioxybenzene is probably due to the proximity of the side ring, just as the *a*-position in naphthalene is the most open to attack.

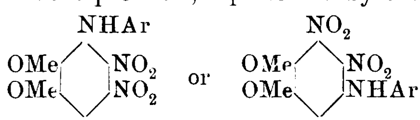
Cardwell and Robinson (A., 1915, i, 134) showed that 5-nitroveratrole yields 5-nitroguaiacol on hydrolysis with hydrobromic acid. Similarly, the diethoxy-compound forms 5-nitro-2-ethoxyphenol. The benzoate of this may be obtained, alternatively, by nitrating 2-benzoyloxyphenetole.

For experimental details, see original. J. C. W.

5-Bromoguaiacol and some Derivatives. ELLEN MARGARET HINDMARSH, ISABEL KNIGHT, and ROBERT ROBINSON (T., 1917, **111**, 940—946).—The methoxy-group of acyl derivatives of guaiacol has a far greater orienting influence than the acyloxy-group, and accordingly, bromination leads to the acyl derivatives of 5-bromoguaiacol. The free phenol behaves normally on further bromination, giving 4:5-dibromoguaiacol. With nitric acid, it reacts to form 5-bromo-4:6-dinitroguaiacol, but no mono-derivative has been obtained. The constitution of this is proved by the conversion of its methyl ether, by means of alcoholic ammonia, into 3:5-dinitro-2:4-diaminoanisole, thus:



The bromine atom in the dimethyl ether is comparatively firmly attached. The reaction with ammonia is very sluggish, and methylamine reacts in a similar way. Aniline and *p*-toluidine, however, give different products, represented by the formulæ



For experimental details, see the original. J. C. W.

1 : 5-Dihydroxynaphthalene. II. OTTO FISCHER [with CONSTANZE BAUER] (*J. pr. Chem.*, 1917, [ii], **95**, 261—266. Compare A., 1916, i, 718).—There are in 1 : 5-dihydroxynaphthalene two positions, namely, 2 and 4, at which substitution takes place readily. It has already been shown that the compound only yields a mononitroso-derivative, in which position 2 is attacked, whilst most diazonium salts also only give monoazo-compounds. Position 4 is usually affected in the latter reaction, but, contrary to other diazonium salts, diazotised phenolic bases attack position 2. The constitutions of the azo-dyes may be determined by reduction to the corresponding amines.

2-Nitroso-1 : 5-dihydroxynaphthalene is reduced by means of phenylhydrazine to *2-amino-1 : 5-dihydroxynaphthalene*, which crystallises in almost colourless, stellate groups, but is very unstable if exposed to air and light in a moist condition. The *hydrochloride* forms pale grey needles, and a sparingly soluble stannichloride is obtained if stannous chloride is the reducing agent. The amine resembles 2-amino-α-naphthol in its behaviour towards ferric chloride in acid solutions. A reddish-violet coloration is produced, which changes to deep reddish-brown on adding more ferric chloride, and finally deep red needles separate.

4-Benzeneazo-1 : 5-dihydroxynaphthalene (*ibid.*) is reduced by stannous chloride to *4-amino-1 : 5-dihydroxynaphthalene hydrochloride*, which gives dark yellow shades, and finally yellow needles, with ferric chloride.

Diazotised *o*-aminophenol couples with 1 : 5-dihydroxynaphthalene to give *2-o-hydroxybenzeneazo-1 : 5-dihydroxynaphthalene*, which is a very dark red powder with green reflex. This, and diamond-black-P.V. (1 : 5-dihydroxynaphthalene-4-azo-2′-phenol-5′-sulphonic acid), give 2-amino-1 : 5-dihydroxynaphthalene on reduction. Diazotised *o*- and *m*-aminobenzoic acids yield *4-o-carboxybenzeneazo-1 : 5-dihydroxynaphthalene* [dark green, lustrous needles, m. p. 257° (decomp.)] and the *4-m-carboxybenzeneazo*-compound (a very dark red powder with green reflex) respectively. J. C. W.

Condensation, under the action of Potassium Hydroxide, of *cyclo*Hexanol with *sec.*-Butyl Alcohol; Synthesis of α-*cyclo*-Hexylbutan-β-ol. MARCEL GUERBET (*Compt. rend.*, 1917, **165**, 559—561. Compare this vol., i, 453).—When *cyclo*hexanol is heated with *sec.*-butyl alcohol and anhydrous potassium hydroxide in a sealed tube at 210—220° for twenty-four hours, it yields *α-cyclohexylbutan-β-ol*, b. p. 126—127°/31 mm., D^0 0·9463, giving an *acetate*, b. p. 129—130°/31 mm., and a *phenylcarbamate*, m. p. 76°. The alcohol when oxidised with chromic acid yields *cyclohexylmethyl ethyl ketone*, $C_6H_{11}\cdot CH_2\cdot COEt$, b. p. 123—124°/31 mm., D^0 0·917, giving a *semicarbazone*, m. p. 145—146°.

W. G.

Preparation of Acylhydroxylamides from the [Oximes] of α-Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1917, **165**, 592—594).—With iodine in the presence of sodium carbonate or

hydrogen carbonate, the oximes of α-ketonic acids undergo oxidation, giving acylhydroxylamides, thus: $CH_2Ph{\cdot}C(CO_2H){:}NOH + O = CO_2 + CH_2Ph{\cdot}CO{\cdot}NH{\cdot}OH$, a secondary reaction also occurring, the oxime being dehydrated, giving a nitrile. In this way, three such acylhydroxylamides have been prepared, namely, *benzoylhydroxylamide*, $COPh{\cdot}NH{\cdot}OH$, m. p. 108°; *phenylacetylhydroxylamide*, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}OH$, m. p. 75°; and *phenylpropionylhydroxylamide*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}OH$, a liquid. These acylhydroxylamides differ from the isomeric hydroxamic acids in that they are not readily hydrolysed, and with alkali do not give substituted carbamides, but are decomposed, giving a mixture of acids.

W. G.

Nitro- and Amino-phenoxyacetic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2188—2224).—An account of the preparation of a large number of these acids and their derivatives. The nitrophenoxyacetic acids may be prepared by Kym's method (compare A., 1897, i, 283) and then reduced to the corresponding amino-acids. A more satisfactory way, particularly for the *p*-amino-acids, is to use Howard's method (compare A., 1897, i, 283), and boil the acetylaminophenol and chloroacetic acid with aqueous sodium hydroxide. The following compounds are described.

o-*Acetylaminophenoxyacetic acid*,

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 153—154° (corr.), which when boiled with hydrochloric acid gave *o*-aminophenoxyacetic anhydride, m. p. 173—173·5° (corr.) (Thate gives 166—167°; compare A., 1884, 1170); m-*aminophenoxyacetic acid*, m. p. 207—208° (decomp.), giving a *hydrochloride* and an *ethyl ester hydrochloride*, m. p. 135—136·5°.

5-*Nitro-2-methylphenoxyacetic acid*, m. p. 177—177·5° (corr.), giving 5-*amino-2-methylphenoxyacetic acid*, m. p. 232° (decomp.). 3-*Nitro-4-methylphenoxyacetic acid*, m. p. 151—154° (corr.), yielding 3-*amino-4-methylphenoxyacetic acid*, m. p. 235—240° (decomp.), giving a *hydrochloride*.

The sodium salt of 5-nitroguaiacol when heated with ethyl chloroacetate at 150° for one and a-half hours yielded *ethyl* 3-*nitro*-6-*methoxyphenoxyacetate*, m. p. 84·5—85° (corr.), which when warmed in aqueous-alcoholic solution with an excess of sodium hydroxide gave the free *acid*, m. p. 184·5—186° (corr.), and this on reduction gave 3-*amino*-6-*methoxyphenoxyacetic acid*, m. p. 222—224° (decomp.), which was also obtained from 5-acetylaminoguaiacol by Howard's method, the intermediate 3-*acetylamino*-6-*methoxyphenoxyacetic acid*, m. p. 208—210° (corr.), being hydrolysed with hydrochloric acid.

p-Aminophenoxyacetic acid gives a *methyl ester hydrochloride*, m. p. 223—225°, and a *methyl ester*, m. p. 65—66° (corr.).

p-*Acetylmethylaminophenoxyacetic acid*,

$$CH_3{\cdot}CO{\cdot}NMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 151—152° (corr.), on hydrolysis yields p-*methylaminophen-*

oxyacetic acid, m. p. 213—214° (decomp.), giving a *nitroso*-compound.

p-*Glycine ethyl ester phenoxyacetic acid*,

$$CO_2Et\cdot CH_2\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

m. p. 173—176° (decomp.), was prepared by boiling *p*-aminophenoxyacetic acid with ethyl chloroacetate and sodium hydroxide in aqueous-alcoholic solution, and on hydrolysis yielded p-*glycinephenoxyacetic acid*, m. p. 177—180° (decomp.), giving a *hydrochloride* and a *dimethyl ester*, m. p. 63·5—64° (corr.).

4-*Acetylamino-2-methylphenoxyacetic acid*, m. p. 202—204·5°, on hydrolysis yielded 4-*amino-2-methylphenoxyacetic acid*, which was also obtained by the reduction of 4-*nitro-2-methylphenoxyacetic acid*, m. p. 127·5—130·5°, with tin and hydrochloric acid. The amino-acid gives a *hydrochloride*, a *methyl ester*, 59·5—60° (corr.), giving a *hydrochloride*, m. p. 195—200° (decomp.), and an *ethyl ester*, m. p. 43—44·5° (corr.), giving a *hydrochloride*, m. p. 185—193° (decomp.).

4-*Acetylamino-3-methylphenoxyacetic acid*, m. p. 165—167·5°, yielded on hydrolysis 4-*amino-3-methylphenoxyacetic acid*, m. p. 217—219° (decomp.), which gave a *methyl ester*, m. p. 105—105·5° (corr.), giving a *hydrochloride*, m. p. 195—200°, and an *ethyl ester*, m. p. 55—55·5° (corr.), giving a *hydrochloride*, m. p. 203—204° (decomp.). The amino-acid, which may also be obtained by the reduction of 4-*nitro-3-methylphenoxyacetic acid*, m. p. 141—143°, when shaken with chloroacetyl chloride in the presence of sodium acetate, gave 4-*chloroacetylamino-3-methylphenoxyacetic acid*, m. p. 159—160·5° (corr.).

p-*Nitroso*-o-*allylphenol*, m. p. 99·5—100° (decomp.), obtained by the addition of acetic acid to a solution of *o*-allylphenol in aqueous sodium hydroxide in the presence of sodium nitrite, on reduction with ammonium sulphide gave 4-*amino-2-allylphenol*, m. p. 112·5—113·5° (corr.), giving an *acetyl* derivative, m. p. 93—93·5° (corr.), which by the usual method yielded 4-*acetylamino-2-allylphenoxyacetic acid*, m. p. 181—183° (corr.), which on hydrolysis gave 4-*amino-2-allylphenoxyacetic acid*, m. p. 193·5—194° (decomp.). A similar series of reactions, starting with *p*-nitroso-*p*-xylenol, gave 4-*acetylamino-2 : 5-dimethylphenol*, m. p. 180—181·5° (corr.), 4-*acetylamino-2 : 5-dimethylphenoxyacetic acid*, m. p. 195—197° (corr.), and 4-*amino-2 : 5-dimethylphenoxyacetic acid*, m. p. 210—215°, giving a *hydrochloride*, a *methyl ester*, m. p. 66·5—67° (corr.), and its *hydrochloride*, m. p. 232—234° (decomp.), and an *ethyl ester*, m. p. 66—66·5°, and its *hydrochloride*, m. p. 205—215° (decomp.).

Acetylaminocarvacrol by the usual method yielded 4-*acetylamino-2-methyl-5-*iso*propylphenoxyacetic acid*, m. p. 190—191·5° (corr.), from which 4-*amino-2-methyl-5-*iso*propylphenoxyacetic acid*, m. p. 225—226°, was prepared, giving a *methyl ester*, 29—30° (corr.), and its *hydrochloride*, m. p. 185—186° (corr.). In a similar manner, *p*-acetylaminothymol gave 4-*acetylamino-3-methyl-6-*iso*propylphenoxyacetic acid*, m. p. 186·5—188° (corr.), and 4-*amino-3-methyl-6-*iso*propylphenoxyacetic acid*, m. p. 204—206° (decomp.),

giving a *methyl ester*, an oil, and its *hydrochloride*, m. p. 169—171°.

2-Bromo-4-acetylaminophenol gave, by the usual method, 2-*bromo*-4-*acetylaminophenoxyacetic acid*, m. p. 216—219·5°, and 2-*bromo*-4-*aminophenoxyacetic acid*, m. p. 230—235°, giving a *hydrochloride* and a *methyl ester*, m. p. 74·5° (corr.), and its *hydrochloride*, m. p. 220—222°.

When *p*-acetylamino-*o*-cresol, in supersaturated acetic acid solution, was brominated by bromine in acetic acid at 35—40°, it yielded 6-*bromo*-4-*acetylamino*-o-*cresol hydrobromide*, m. p. 194—196° (decomp.), which with sodium acetate in aqueous solution gave the free acetylaminobromocresol (compare Janney, A., 1913, i, 854). The hydrobromide yielded 6-*bromo*-4-*acetylamino*-2-*methylphenoxyacetic acid*, m. p. 216—216·5° (corr.), and 6-*bromo*-4-*amino*-2-*methylphenoxyacetic acid*, m. p. 223° (decomp.), giving a *methyl ester*, m. p. 59° (corr.), and its *hydrochloride*, m. p. 245—250° (decomp.).

4-Acetylaminoguaiacol gave 4-*acetylamino*-6-*methoxyphenoxyacetic acid*, m. p. 190—191°, and 4-*amino*-6-*methoxyphenoxyacetic acid*, m. p. 190° (decomp.), giving an *ethyl ester* and its *hydrochloride*, m. p. 180—186°.

o-Aldehydophenoxyacetic acid, when added gradually to nitric acid (D 1·52) at 5°, yielded 4-*nitro*-6-*aldehydophenoxyacetic acid*, m. p. 190—192° (corr.), which gave a *phenylhydrazone*, decomp. 222°, and on oxidation with potassium permanganate in the presence of sodium carbonate, 4-*nitro*-6-*carboxyphenoxyacetic acid*, m. p. 238—240° (decomp.), which when boiled with alcohol and sulphuric acid yielded *ethyl* 4-*nitro*-6-*carbethoxyphenoxyacetate*, m. p. 75—76° (corr.). The free nitro-acid or its ester, when reduced with tin and hydrochloric acid in alcoholic solution, yielded 4-*amino*-6-*carboxyphenoxyacetic acid*, giving an *ethyl ester*, m. p. 74—76° (corr.), and its *hydrochloride*, m. p. 156—157°.

2-Hydroxy-5-acetylaminoacetophenone, when boiled with chloroacetic acid and aqueous sodium hydroxide, gave 4-*acetylamino*-6-*acetylphenoxyacetic acid*, m. p. 223—226° (decomp.), which on hydrolysis yielded 4-*amino*-6-*acetylphenoxyacetic acid*, m. p. 145° (decomp.), giving a *methyl ester*, m. p. 141—142·5° (corr.), and its *hydrochloride*, m. p. 204—207° (decomp.).

o-Phenylenedioxyacetic acid, on nitration with nitric acid (D 1·4) at 25°, gave 4(?)-*nitro*-o-*phenylenedioxyacetic acid*, m. p. 181—183° (corr.), which was reduced by tin and hydrochloric acid, giving *amino*-o-*phenylenedioxyacetic acid*, m. p. 243—245° (decomp.).

A number of compounds similar to the aminophenoxyacetic acids and containing condensed nuclei were also prepared. 4-*Acetylamino*-1-*naphthoxyacetic acid*, m. p. 233—234°, giving 4-*amino*-1-*naphthoxyacetic acid*, m. p. 220—224° (decomp.). 8-*Acetylamino*-5-*hydroxyquinoline*, m. p. 221—223°, gives 8-*acetylamino*-5-*quinolyloxyacetic acid*, m. p. 255° (decomp.), giving 8-*amino*-5-*quinolyloxyacetic acid*, m. p. 225° (decomp.).

5-*Amino*-8-*hydroxyquinoline dihydrochloride*, m. p. 245° (decomp.), obtained by the reduction of the corresponding nitroso-

compound, gave 5-*acetylamino*-8-*hydroxyquinoline*, m. p. 221—222°, which yielded 5-*acetylamino*-8-*quinolyloxyacetic acid*, m. p. 253—255° (decomp.), giving a *nitrate*, m. p. 225—230° (decomp.), and on hydrolysis 5-*amino*-8-*quinolyloxyacetic acid dihydrochloride*, m. p. 160—162° (decomp.), giving a *methyl ester*, 176—177° (corr.).

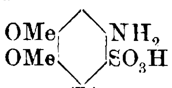
Two aminophenoxybutyric acids were also prepared, as follows. *o*-Acetylaminophenol, when boiled for three hours in alcoholic solution with sodium hydroxide and trimethylene bromide, yielded a small amount of *propylenebis*-(o-*acetylaminophenyl*) *ether*,

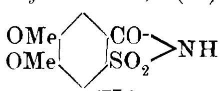
$$COMe{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}COMe,$$

m. p. 193·5—194·5° (corr.), and as principal product o-*acetylaminophenoxypropyl bromide* [o-*acetylaminophenyl* γ-*bromopropyl ether*], $COMe{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, m. p. 62—62·5° (corr.), which in boiling alcoholic solution with potassium cyanide gave o-*acetylaminophenoxybutyronitrile*, m. p. 89—90° (corr.), and this when boiled with hydrochloric acid yielded o-*amino*-γ-*phenoxybutyric acid hydrochloride*, m. p. 180—182°. The free *amino-acid*, m. p. 54—57°, gives a *methyl ester*, m. p. 45—45·5°. A similar series of compounds was prepared starting with *p*-acetylaminophenol. p-*Acetylaminophenoxypropyl bromide*, m. p. 133—135°; p-*acetylaminophenoxybutyronitrile*, m. p. 98—100°; p-*amino*-γ-*phenoxybutyric acid hydrochloride*, m. p. 191—194°, and its free *amino-acid*, m. p. 145·5—146° (corr.).

Practically all the aminophenoxyacetic acids and their esters give colours with ferric chloride, and those containing primary amino-groups are readily diazotised, and then couple with R-salt to give soluble dyes of varying shades of red. W. G.

Veratricsulphinide. JANET FORREST MCGILLIVRAY BROWN, and ROBERT ROBINSON (T., 1917, **111**, 952—958).—Veratrole and homoveratrole react smoothly with chlorosulphonic acid. Through the sulphonyl chloride, the former has been converted into 5-aminoveratrole-4-sulphonic acid (I), and the latter into veratric-6-sulphinide, or "dimethoxysaccharin," (II):


(I.)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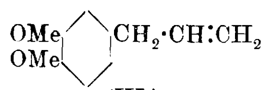

(III.)

Eugenyl methyl ether (III) occurs in large quantities in the Huon Pine of Tasmania, and it was thought that an outlet might be found for it by converting it into the above "saccharin" derivative. It does not react with chlorosulphonic acid in the normal way, however, and, moreover, the veratricsulphinide is not sweet.

Other veratrole derivatives behave abnormally with chlorosulphonic acid. For example, piperonylonitrile yields the di-imide of an anthraquinone derivative, of the formula:

$$CH_2{:}O_2{:}C_6H_2{<}{\begin{matrix}C({:}NH)\\C({:}NH)\end{matrix}}{>}C_6H_2{:}O_2{:}CH_2.$$

For experimental details, see the original. J. C. W.

Salts and Esters of *d*-Camphoric Acid. H. Thoms and P. Runze (*Ber.*, 1917, **50**, 1217—1221).—Camphoric acid exhibits a great tendency to form normal salts, so that, if treated with one equivalent proportion of sodium carbonate, it does not yield the sodium hydrogen salt, but a mixture of the disodium salt and free acid. Attempts have been made, however, to prepare soluble ester-salts, using phenols as one component, in view of their probable value in therapeutics.

Many aryl hydrogen camphorates were prepared by Schryver (T., 1899, **75**, 661). To these are now added the cresol derivatives, the *tolyl hydrogen* d-*camphorates*, as follows: *ortho-*, glistening needles, m. p. 127°, $[\alpha]_D^{20}$ +66·18°; *meta-*, m. p. 98°; *para-*, glistening crystals, m. p. 102—103°.

Attempts to convert the *o*-tolyl ester into sodium or potassium *o*-tolyl camphorate by exact neutralisation result in the formation of the di-alkali salts, free *o*-cresol, and free camphoric acid. If the solution of the ester in alcohol and ether is mixed with alcoholic ammonia, however, *ammonium* o-*tolyl camphorate* is precipitated. The *methylammonium* and *diethylammonium* (m. p. 109—110°) salts can be obtained in the same way. The ammonium salts are decomposed by boiling alcohol. *Cupric* o-*tolyl camphorate*, $(C_6H_4Me\cdot CO_2\cdot C_8H_{14}\cdot CO_2)_2Cu$, can also be prepared by immediately adding copper sulphate to a mixture of the ester and one equivalent of sodium hydroxide. It is decomposed by boiling water into copper camphorate, camphoric acid, and *o*-cresol.

No salts of the above type could be obtained with cyclic bases, and an attempt to prepare *o*-tolyl camphoranilate resulted in the formation of free camphoranilic acid, m. p. 204°. J. C. W.

Demonstration of the Scission of Salts of Organic Acids by means of Conductivity Determinations. H. Thoms and G. K. W. Zehrfeld (*Ber.*, 1917, **50**, 1221—1227).—Küster has shown that in the case of many of the mono- and di-basic acids exact titrations can be made by determining the points of abrupt change (often minima) in the conductivity curve as alkali is added to the acid, but he pointed out that the critical change sets in too soon in the case of some weak acids (A., 1903, ii, 611; 1905, ii, 55). Camphoric acid is a good example of the latter class. If sodium hydroxide is gradually added to a solution of the acid, the conductivity falls for a brief interval, but very soon proceeds to rise until the acid is neutralised. For a time, therefore, the solution contains a substance of lower conductivity than the free acid, which can only be sodium hydrogen camphorate. Küster would have explained the subsequent quick change in the conductivity by assuming that ions of this salt were rapidly appearing in place of undissociated acid molecules, but there is another interpretation. From a solution of camphoric acid with one equivalent of alkali, that is, apparently, a solution of the acid salt, ether will extract nearly half of the acid in the free state, leaving the normal salt (see following abstract). In other words, as Jungfleisch and Landrieu also demonstrated (A.,

1914, i, 416), sodium hydrogen camphorate is decomposed by water into the normal salt and free acid. The change in conductivity is therefore due to a new grouping of the ions already present. The change sets in later if the solutions are more concentrated, which supports the view that the effect is due to the action of water.

J. C. W.

Scission of Acid Salts into Normal Salts and Free Acids in Aqueous Solutions. H. THOMS and TH. SABALITSCHKA (*Ber.*, 1917, **50**, 1227—1235).—Acid salts of dibasic acids, MHX, in aqueous solutions give the ions M˙ and HX′, and the latter ion may be resolved further into H˙ and X″. These ions may subsequently re-unite in all possible ways, to give molecules of the normal or acid salt and free acid. The tendency will be towards the production of the least soluble or least dissociated molecules, under the given conditions. If the new product is removed, the new change will continue in the new direction.

In the case of potassium hydrogen sulphate, for example, it might be possible for potassium sulphate to crystallise out if its solubility-product is surpassed. This has actually been achieved by repeatedly precipitating the salt from a solution of the acid sulphate by means of alcohol. After four precipitations, pure potassium sulphate was obtained.

On the other hand, it is possible in the case of some organic acids to remove the free acid by extraction with ether, and so to obtain the neutral salt. In the case of the alkali hydrogen camphorates, the salts are already very largely resolved into normal salts and free acids, so that one extraction with ether will remove nearly half of the total amount of acid. The influence of the metallic ion is not very great, but ether will extract slightly more acid from a potassium hydrogen camphorate solution than from a sodium, lithium, or ammonium salt solution under the same conditions. *iso*Camphoric and *iso*phthalic acid salts behave similarly. The same is true for sodium hydrogen phthalate solutions, but here the quantitative control of the experiments is weakened by two other facts. First, phthalic acid so easily changes into the anhydride that ethereal solutions lose water on evaporation, and secondly, normal sodium phthalate is hydrolysed by water and so yields up some phthalic acid to ether.

Ether does not extract oxalic acid from solutions of potassium hydrogen oxalate, but does from the quadroxalate, leaving the acid salt. Apparently, the $CO_2H{\cdot}CO_2'$– ion does not dissociate to any appreciable extent, or, rather, the K˙, H˙, and $(CO_2)_2''$ ions do not tend to reunite to form new molecules. J. C. W.

Condensation of Ethyl Oxalate with Ethyl Ethoxycrotonate, Ethoxypropene, and Acetonediethylacetal. WILHELM WISLICENUS and KARL SCHÖLLKOPF (*J. pr. Chem.*, 1917, [ii], **95**, 269—298).—Ethyl oxalate and ethyl β-ethoxycrotonate

react in the presence of potassium ethoxide to form a deep red salt, thus:

$$OEt\cdot CMe{:}CH\cdot CO_2Et + C_2O_4Et_2 + KOEt = CO_2Et\cdot C{<}\begin{matrix} CO\text{——}C\cdot OK \\ \quad\quad\ \ \| \\ C(OEt)\cdot CH \end{matrix} + 3EtOH.$$

When this is acidified, an ethyl radicle is eliminated and an ester is produced which reacts as a triketone or mono-enol, thus:

$$CO_2Et\cdot CH{<}\begin{matrix} CO\cdot CO \\ \quad | \\ CO\cdot CH_2 \end{matrix} \quad \text{or} \quad CO_2Et\cdot CH{<}\begin{matrix} CO\cdot C\cdot OH \\ \quad \| \\ CO\cdot CH \end{matrix} \quad \text{or}$$
(I.) (II.)

$$CO_2Et\cdot C{<}\begin{matrix} C(OH)\cdot CO \\ \quad\quad | \\ CO\text{——}CH_2 \end{matrix}$$
(III.)

The properties and reactions of this ester, "ethyl oxalylacetoacetate," form the chief feature of this communication.

The above-mentioned salt, *potassium ethyl 4-hydroxy-2-ethoxy-*$\Delta^{1:3}$-cyclo*pentadiene-5-one-1-carboxylate*, crystallises in deep purplish-red bundles of microscopic needles, m. p. 240° (decomp.). It decomposes slowly in contact with cold water, better on boiling with 96% alcohol, yielding the potassium salt of *4-ethoxy-α-pyrone-6-carboxylic acid*, $CO_2K\cdot C{<}\begin{matrix} O\text{———}CO \\ CH\cdot C(OEt) \end{matrix}{>}CH$. The free acid crystallises in small, colourless needles, which melt with evolution of gas when plunged in a bath at 150°, then solidify again, and finally melt at 164—166°. The *ethyl* ester, m. p. 84—86°, changes into the original red potassium salt when mixed with potassium ethoxide, and reacts with ammonia to form *ethyl 2:4-dihydroxypyridine-6-carboxylate*, m. p. 198—200°.

The *enolic* form of "*ethyl oxalylacetoacetate*," the "α"-modification (II) or (III), is best obtained by mixing the red salt with concentrated sulphuric acid in the presence of ether, and then extracting the solid ester from the potassium hydrogen sulphate by means of ether. It crystallises in pale yellow needles, m. p. 145—150° (decomp.), gives the typical ferric chloride and Laubenheimer reactions, yields a yellow precipitate with potassium ethoxide, but does not form esters. The β-modification, *ethyl* cyclo*pentane-2:4:5-trione-1-carboxylate* (I), is obtained by boiling the enol with water, cooling, and adding a large excess of sulphuric acid. It crystallises in microscopic, yellow, elongated leaflets, m. p. 105—110° (decomp.), gives first a yellow and then a red precipitate with potassium ethoxide, and decomposes on boiling with solvents.

The two esters behave in a remarkable manner when attempts are made to isolate their salts. The α-form gives a normal, very pale yellow *pyridine* salt, $C_8H_8O_5,C_5H_5N,3H_2O$, m. p. 55° (anhydrous, m. p. 98°), when mixed with the base in moist ethyl acetate, and this yields the enol again when mixed with concentrated sulphuric acid and ether. When boiled with alcohol, this salt changes into an abnormal, orange-red *salt*, $C_{16}H_{14}O_9,C_5H_5N$, from which the β-form is recoverable. This salt may be obtained by boiling the α-form, but

better the β-modification, with pyridine and alcohol or acetone, thus: $2C_8H_8O_5 + C_5H_5N = C_{16}H_{14}O_9,C_5H_5N + H_2O$. Either ester yields a corresponding abnormal *potassium* salt, $C_{16}H_{13}O_9K$ (bundles of yellow needles), when warmed with aqueous-alcoholic potassium hydroxide, and the β-form gives the similar *ammonium* salt (golden-yellow, felted needles) with alcoholic ammonia; these give the β-ester on acidifying.

The α-ester reacts with one molecular proportion of phenylhydrazine to form a *phenylhydrazone* (A); this crystallises in small,

$$\underset{\text{(A.)}}{NHPh{\cdot}N{:}C{<}\begin{array}{l}C(OH){=\!=}CH\\CH(CO_2Et){\cdot}CO\end{array}};\qquad \underset{\text{(B.)}}{NPh{<}\begin{array}{l}CO{\cdot}CH{-}CO\\N{=}C{\cdot}C(OH)\end{array}{>}CH}.$$

yellow tablets, m. p. 184—186° (decomp.), and changes into a *pyrazolone* derivative (B), stellate groups of yellow needles, m. p. about 190° (decomp.), on boiling with glacial acetic acid. With two molecular proportions of phenylhydrazine, the ester yields an additive *compound* of phenylhydrazine and the above phenylhydrazone; this crystallises in pale yellow needles, m. p. 148° (decomp.), and changes into a *diphenylhydrazone* of "ethyl oxalylacetoacetate,"

$$CO_2Et{\cdot}CH{<}\begin{array}{l}C({:}N{\cdot}NHPh){\cdot}C{\cdot}OH\\C({:}N{\cdot}NHPh){\cdot}CH\end{array},$$

when boiled with methyl alcohol. The same compound is formed as a precipitate when a solution of the base in dilute acetic acid is added to an aqueous solution of the original red potassium salt; it crystallises in very pale brown, rhombic leaflets, m. p. 198—202° (decomp.), which change in contact with methyl alcohol into curved filaments (additive compound). The diphenylhydrazone also changes into an *isomeride*, deep, greenish-yellow tablets, m. p. 198—200°, when boiled with glacial acetic acid or xylene, but not if heated alone. The β-ester forms a sparingly soluble, dark red *phenylhydrazone*.

A solution of the original red salt gives a precipitate of a *dianilino*-derivative of "ethyl oxalylacetoacetate,"

$$CO_2Et{\cdot}C{\lessdot}\begin{array}{l}C({:}NPh){-}{-}C{\cdot}OH\\C(NHPh){\cdot}CH\end{array}\quad\text{or}\quad CO_2Et{\cdot}C{\lessdot}\begin{array}{l}CO{-\!-\!-\!-}C{\cdot}NHPh\\C(NHPh){\cdot}CH\end{array};$$

this crystallises in dark, ruby-red, elongated, glistening leaflets. The same salt reacts with *o*-phenylenediamine to form a *phenazine* of "ethyl oxalylethoxycrotonate," yellowish-red needles, m. p. 183—185° (decomp.):

$$C_6H_4{<}\begin{array}{l}N{:}C{\cdot}C(CO_2Et){:}C{\cdot}OEt\\N{:}C{-\!-\!-\!-\!-\!-}CH_2\end{array}\quad\text{or}\quad C_6H_4{<}\begin{array}{l}N{=}C{\cdot}C(CO_2Et){:}C{\cdot}OEt\\NH{\cdot}C{=\!=\!=\!=}CH\end{array}$$

The above α-oxalylacetoacetic ester also yields a *phenazine*, $C_{14}H_{12}O_3N_2$, which crystallises in bundles of slender, yellow needles, decomp. 210—220°, and exhibits a bright, bluish-green fluorescence in organic solvents. This phenazine differs from the foregoing one by the ethyl radicle of the ethoxyl group, and it can also be obtained by boiling the first phenazine with dilute acetic acid.

The initial red salt, or an alkaline solution of the above α-ester, also reacts with benzenediazonium chloride to form *ethyl* 3-*hydroxy*-4-*benzeneazo*-Δ^3-cyclo*pentene*-2 : 5-*dione*-1-*carboxylate* (" *ethyl benzeneazo-oxalylacetoacetate* "), $CO_2Et \cdot CH <\begin{matrix} CO \cdot C \cdot OH \\ CO \cdot C \cdot N : NPh \end{matrix}$, which crystallises in dark red, glistening, flat needles, decomp. about 180°.

Ethyl oxalate also combines with β-ethoxypropene (*iso*propenyl ethyl ether) and acetonediethylacetal ($\beta\beta$-diethoxypropane) in the presence of potassium ethoxide, but the product is the *dipotassium* salt of ethyl acetonedioxalate (compare Willstätter and Pummerer, A., 1904, i, 973). J. C. W.

Action of Halogens on Piperonaldehyde. ANNIE MARY BLEAKLY ORR, ROBERT ROBINSON, and MARGARET MARY WILLIAMS (T., 1917, **111**, 946—952).—If piperonaldehyde is treated with bromine or chlorine in neutral solvents, excellent yields of the 6-halogenopiperonaldehydes are obtained, but displacement of the aldehydo-group takes place to a considerable extent if glacial acetic acid is used as the solvent, the 4 : 5-dihalogenocatechol methylene ethers being formed as well. The aldehydo-group is also displaced if the halogenopiperonaldehydes are nitrated. Similarly, the carboxyl groups in piperonylic and 6-chloropiperonylic acids are displaced on adding bromine or chlorine to sodium carbonate solutions of these acids.

Piperonaldehyde has been converted into its corresponding alcohol and acid by the Cannizzaro reaction.

For experimental details, see the original. J. C. W.

A New Method for Preparing Cyclic Ketones. III. and IV. ALFRED SCHAARSCHMIDT (*Ber.*, 1917, **50**, 1356—1359, 1360—1362. Compare this vol., i, 285).—Polemical. Replies to Ullmann (this vol., i, 342). J. C. W.

Homoeriodictyol. O. A. OESTERLE and R. KUENY (*Arch Pharm.*, 1917, **255**, 308—314).—Power and Tutin's homoeriodictyol (T., 1907, **91**, 887), named eriodictyonone by Mossler (A., 1907, i, 947; ii, 292), has been regarded as a hydrindene derivative by the latter and as 2 : 4 : 6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone by Tutin (T., 1910, **97**, 2054). Further evidence in support of the latter view has been obtained by the authors. Hesperetin, which is isomeric with homoeriodictyol, has already been converted into 5 : 7 : 3′-trihydroxy-4′-methoxyflavone (luteolin methyl ether, m. p. 253—254°) by the authors (*Arch. Pharm.*, 1915, **253**, 383). So also homoeriodictyol, for which the authors find m. p. 218° (Power and Tutin give 223°; Mossler, 214—215°), has been converted into a new luteolin monomethyl ether, which is 5 : 7 : 4′-*trihydroxy*-3′-*methoxyflavone*,

$$OMe \cdot C_6H_3(OH) \cdot C <\begin{matrix} \text{———O} \\ CH \cdot CO \end{matrix}> C_6H_2(OH)_2,$$

citron-yellow needles, m. p. 324—325° (decomp.), the positions of the substituents being determined by the nature of the fission pro-

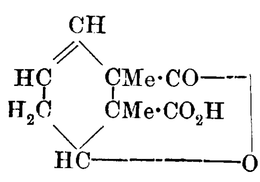
ducts (phloroglucinol and ferulic acid) of homoeriodictyol. The substance is obtained as follows. Tetra-acetylhomoeriodictyol, m. p. 154° (Power and Tutin give the same m. p.; Mossler gives 158°), is converted by bromine in chloroform into a crude bromide, a hot alcoholic solution of which is treated with 50% potassium hydroxide and subsequently with water. The new luteolin monomethyl ether is precipitated from the solution by hydrochloric acid, and is best purified through its *triacetate*, $C_{16}H_9O_6Ac_3$, faintly yellow needles, m. p. 215—216°. The triacetate yields luteolin when boiled for nine hours with equal volumes of glacial acetic acid and hydriodic acid, D 1·96.

The authors direct attention to the great similarity between 5 : 7 : 4′-trihydroxy-3′-methoxyflavone and Tutin and Clewer's chrysoeriol (T., 1909, **95**, 81), and hope to prove that the two substances are identical. C. S.

Cantharidin. VIII. Pyrogenic Decomposition of Barium Cantharate. J. GADAMER (*Arch. Pharm.*, 1917, **255**, 315—337).—The only remaining point at variance with Rudolph's formula of cantharidin is the formation of *a*-hemellithylic acid by the pyrogenic decomposition of barium or calcium cantharate (compare Gadamer, this vol., i, 659), and this discrepancy now receives attention.

An optically not quite pure, lævorotatory *d*-cantharic acid, $[\alpha]_D$ −70°, is evaporated to dryness with a concentrated aqueous solution of rather more than two equivalents of barium hydroxide, and the residue is heated at about 380° for ten to twenty minutes in a current of dry hydrogen. The products are: (1) water; (2) an oil, consisting of impure cantharene; and from the residue after acidification (3) acids volatile with steam, and (4) acids non-volatile with steam. The acids under (3) are separated into (*a*) those easily soluble in water, and (*b*) those sparingly soluble in water. Two of the former are suspected from their odour to be angelic or *a*-methylbutyric acid and *iso*butyric acid, but no acids in the pure state could be isolated. The author indicates the possibility of the formation of these acids from cantharic acid (formula I).

From the mixture of acids obtained under 3*b*, two acids have been isolated in a pure state, namely, *a*-hemellithylic and *p*-xylic (3:4-dimethylbenzoic) acids, in the proportion of 10:1. The



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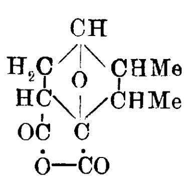

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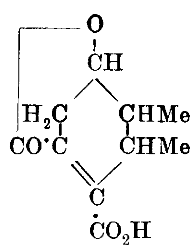


(III.)

formation of these two acids would be easily explicable if cantharidin and cantharic acid contained four side chains, namely, two methyl groups in the ortho-position and also two carboxyl groups in the ortho-position to one another, as, for example, in formulæ II (cantharidin) and III (cantharic acid). The objection to any such formulæ is, however, that cantharidin must have a symmetrical structure in consequence of its formation from hydrobromocantharic acid (Gadamer, A., 1915, i, 432). There remains, therefore, no alternative but to assume that a migration of radicles (carboxyl groups) occurs during the pyrogenic decomposition of barium cantharate, and the author indicates how α-hemellithylic and *p*-xylic acids could be produced, by such migrations and by loss of hydrogen, from cantharic acid of the accepted formula (I).

The acids under (4) are amorphous and contain unsaturated constituents. After reduction by the Paal-Skita-Mannich method, the bulk of the mixture remains unchanged (and from it nothing of definite character has been isolated), but from the reduced portion an acid, m. p. 54·5°, has been obtained, which may be myristic acid, but is more probably α-methylmyristic acid. C. S.

Synthesis of a Crystalline β-*iso*Curcumin. GUSTAV HELLER (*Ber.*, 1917, **50**, 1244—1247. Compare A., 1915, i, 417).—A second isomeride of *iso*curcumin has been obtained from the product of the condensation of vanillin with acetylacetone. It occurs to the extent of 1—2% of the vanillin used, is sparingly soluble in benzene, and crystallises well only from acetic acid, with which it forms a compound, $3C_{21}H_{20}O_6,C_2H_4O_2$. This β-iso*curcumin*, m. p. 111—112°, dissolves in concentrated sulphuric acid with bright red colour and vivid blue fluorescence, and in alkali carbonates and hydroxides with much brighter red colour than that given by curcumin. It is not transformed into curcumin even at 150°, and it does not give metallic lakes, for example, with ferric chloride. Curcumin is enolic and α-*iso*curcumin probably a mixture (*ibid.*), β-*iso*curcumin is therefore to be regarded as the pure diketone, $CH_2[CO{\cdot}CH{:}CH{\cdot}C_6H_3(OH){\cdot}OMe]_2$. J. C. W.

Periodides in the Coumarin Series. H. SIMONIS (*Ber.*, 1917, **50**, 1137—1142).—Dox and Gaessler (this vol., i, 346) have recently described a compound, $(C_9H_6O_2)_4I_2$, as the product of the action of iodine and potassium iodide on coumarin. It is now shown that potassium enters into the composition of this substance, and that it is really the salt of the acid, $4C_9H_6O_2,HI,I_3$, which Morgan and Micklethwait obtained by dissolving coumarin in hydriodic acid containing iodine (T., 1906, **87**, 868). The potassium iodide can be replaced by other alkali iodides or bromides, or by mercuric iodide, and alkyl derivatives of coumarin, provided that the pyrone ring is intact, give similar compounds.

The following coumarin *periodides* are described:

$$4C_9H_6O_2,KI,I_3,H_2O,$$

bronze-green, scintillating needles, m. p. 87—89°, transformed by fuming hydrochloric acid into Morgan and Micklethwait's com-

pound; 4Cou.,NaI,I_3, violet needles with coppery lustre, m. p. 86—87°; 4Cou.,LiI,I_3, bronze-green, m. p. about 38°;

4Cou.,RbI,I_3,H_2O,

crystals with the colour of Spanish flies, m. p. 86—87°; 4Cou.,CsI,I_3,H_2O, greenish-brown, iridescent needles, m. p. 72—73°; 4Cou.,KI,HgI_2,I_2, bronze-brown, woolly needles, m. p. 96°; 4Cou.,KBr,I_3, golden-green needles, m. p. 74—76°, leaves potassium bromide on distillation.

3-Methylcoumarin gives a *compound*, $4C_{10}H_8O_2,KI,I_3,H_2O$, spinach-green needles, m. p. 100°, and 4 : 7-dimethylcoumarin yields the *substance*, $4C_{11}H_{10}O_2,KI,I_3$, in long, dark green needles, m. p. 115°. J. C. W.

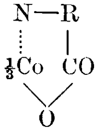
Researches on Pseudo-bases. II. Some Berberine Derivatives and Remarks on the Mechanism of the Condensation Reactions of Pseudo-bases. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1917, **111**, 958—969. Compare T., 1914, **105**, 1456).—The analogy between berberine and cotarnine has been spectrochemically demonstrated by Tinkler (T., 1911, **99**, 1340) and confirmed in the case of their condensation products with acetone by Pyman (*ibid.*, 1694). Further condensation products have now been obtained, which, although much less stable than the corresponding cotarnine and hydrastinine compounds, only serve to strengthen the analogy. Compounds of the types ψ-B–CN, ψ-B–OMe, ψ-B–CH_2Bz, and ψ-B–$CH_2\cdot NO_2$ are described. For experimental details, see the original.

The mechanism of these pseudo-base condensations is discussed in the light of a theory which involves the conjugated partial dissociation of the reacting substances (compare Baly's "opening up the molecular force fields"), followed by direct union, and then re-distribution of the affinities within the new system. The theory is extended to a discussion of the bromination of ketones, and diazo-coupling. J. C. W.

The Alkaloids of the Calabar Bean. VI. Constitution of Geneserine. Transformation of Eserine into Geneserine. MAX POLONOVSKI (*Bull. Soc. chim.*, 1917, [iv], **21**, 191—200. Compare A., 1916, i, 284).—From a further consideration of the properties of eserine and geneserine and a study of the oxidation of eserine, the author now considers geneserine to be an eserine oxide, eserine having the constitution $NMe{:}C_{12}H_{14}N\cdot O\cdot CO\cdot NHMe$, and geneserine, $O{:}NMe{:}C_{12}H_{14}N\cdot O\cdot CO\cdot NHMe$. Eserine, when oxidised in alcoholic solution by hydrogen peroxide, yields geneserine, and eserethol, under similar conditions, yields geneserethol. When eserine is oxidised by potassium permanganate in the presence of dilute sulphuric acid or by dilute nitric acid, partial decomposition occurs, methylamine being liberated. W. G.

Internally Complex Salts. XV. Isomerism and Absorption of Light of Internally Complex Salts. H. LEY and K. FICKEN (*Ber.*, 1917, **50**, 1123—1137).—The optical properties of some salts of amino-acids are discussed.

I. According to Werner's theory, internally-complex salts of the type $M'''(RX)_3$ should exist as *cis*- and *trans*-isomerides, and such are known in the case of the red and violet cobaltiglycines (A., 1909, i, 886) and cobalti-α-alanines (A., 1912, i, 243). To these are now added red and violet cobaltic picolinates. The question is considered whether stereoisomeric forms of each isomeride should not exist. It can easily be demonstrated with a model that the three ring-systems attached to a tervalent atom, as in the annexed formula, could be so arranged in space as to provide for such stereoisomerism. However, the above red and violet salts are so indifferent that no hope of resolving them into possible optical isomerides can be entertained, but it was thought that it might perchance be possible to isolate such compounds if an optically active amino-acid were used at the outset. Accordingly, *cobaltic* salts of *d*-*alanine* have been prepared, but only one form of each geometric isomeride has been found. The red salt forms thin needles, $[M]_{red}$ $-472°$, in 50% sulphuric acid, and the violet salt, which is soluble in boiling 9% sulphuric acid, crystallises in rhombic tablets, $[M]_{red}$ $+1330°$. The solutions of these salts in sulphuric acid do not change colour, but become optically inactive in the course of two years.



II. The following salts of picolinic acid have been prepared. The cupric salt crystallises in deep blue needles or bluish-violet leaflets, both with $2H_2O$. The *cobaltic* salt can be obtained in two forms; the violet salt, $Co(C_6H_4O_2N)_3,H_2O$, crystallises in microscopic, elongated, hexagonal leaflets; the pale red salt, $2H_2O$, forms extremely slender needles which are very sparingly soluble in water, and it can be converted into the violet salt by heating with 25% acetic acid in a sealed tube at 170—180°. The *chromic* salt exists in red needles, with $1H_2O$, sparingly soluble in water, and in insoluble, blue crystals, $\frac{1}{2}H_2O$. The *platinous* salt is extremely stable, and is known only in the form of pale yellow needles.

The cobaltic salts of the amino-acids behave in a curious manner towards sodium hydroxide. Both red and violet forms are hydrolysed by the dilute alkali to cobaltic hydroxide, the violet salts also with concentrated solutions. The red forms of the cobaltic salts of glycine, alanine, and picolinic acid, however, dissolve in concentrated sodium hydroxide to give deep blue solutions resembling those of cobaltous salts.

III. The absorption spectra of red and violet cobaltic picolinates closely resemble those of the salts of glycine and alanine. The characteristic band of picolinic acid ($1/\lambda = 3800$ recip. Å.U.) is not exhibited; both show a band at $1/\lambda = 2700$, and another at about 1950, but the extinction in the latter case is stronger for the red form. Cobaltous picolinate, however, shows the characteristic band of the acid, but, compared with cobaltous acetate or sulphate, its chief absorption band is displaced slightly towards the short-wave end of the spectrum (1960 compared with 2080), and the extinction is much greater. The cobaltous picolinate is, therefore, also an

internally-complex salt, but of a much weaker character than the cobaltic salts. Whilst, for example, the cobaltic salts are stable towards concentrated acids, the cobaltous salt is decomposed, thus: $CoX_2 + 2HCl = CoCl_2 + 2HX$. J. C. W.

Chromoisomerism of Acridinium Salts. A. HANTZSCH (*Ber.*, 1917, **50**, 1204—1213. Compare A., 1916, i, 835).—A continuation of the controversy with Kehrmann (compare this vol., i, 221).

Some misapprehension seems to exist as to what Hantzsch means by "chromoisomerism." He uses the term in a temporary sense only, with reference to isomerides which for the time being are only known to differ in colour, and until chemical, structural differences are revealed which would entitle them to other descriptions.

In the case of the phenylmethylacridinium sulphites, it is claimed that there is no evidence to show how they differ structurally, and so they are still called "chromo-isomerides." They have been re-investigated, and it is described how the following salts may be prepared: *yellow* series: anhydrous sulphite, hydrate (nH_2O?), compound with $1C_2HCl_5$; *brown* series: anhydrous salt; B,H_2O; B,EtOH; B,2EtOH; $B,CHCl_3$; and B,nC_2HCl_5?; *green* series: anhydrous salt; $B,3H_2O$; B,1 and 1·5EtOH; $B,CHCl_3$; and B,1 and $2C_2HCl_5$. J. C. W.

Constitution of Isatin Salts. GUSTAV HELLER (*Ber.*, 1917, **50**, 1199—1202. Compare this vol., i, 219).—A reply to Claasz (this vol., i, 413). Claasz stated that *N*- and *C*-metallic salts are incompatible with water, but it is shown that the *N*-sodium and *N*-potassium salts of isatin can actually be obtained as precipitates, under certain conditions, from alcoholic solutions containing small quantities of water. J. C. W.

Theory of the Oxidation of Benzidine in its Significance for Peroxydase Investigations. W. MADELUNG (*Ber.*, 1917, **50**, 1182—1187. Compare this vol., i, 285).—Polemical. A reply to Woker (this vol., i, 62, 485). J. C. W.

Dindole. GUSTAV HELLER (*Ber.*, 1917, **50**, 1202—1203. Compare Ruggli, this vol., i, 586).—Dindole is obtained in good yield by the gradual addition of zinc dust to an acetic acid solution of *oo'*-dinitrobenzil (Kliegl and Haas, A., 1911, i, 433). It is identical with Golubev's "di-iminotolane." J. C. W.

Action of *p*-Nitroso-bases on Hydrazines. II. OTTO FISCHER [with M. CHUR] (*J. pr. Chem.*, 1917, [ii], **95**, 266—269. Compare A., 1915, i, 907).—The product of the action of semicarbazide on *p*-nitrosodimethylaniline, namely, *p*-dimethylaminobenzenediazoxycarbamide, $NMe_2·C_6H_4·N_2O·NH·CO·NH_2$, decomposes on boiling with 20% sulphuric acid according to the equation $C_9H_{13}O_2N_5 + 2H_2O = N_2 + CO_2 + 2NH_3 + NMe_2·C_6H_4·OH + O$.

J. C. W.

Hydrazides and Azides of Sulphocarboxylic Acids. I. Action of Hydrazine on Ethyl *o*-Aminosulphonylbenzoate. ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **95**, 312—326).—The action of hydrazine on ethyl *o*-aminosulphonylbenzoate,

$$NH_2\cdot SO_2\cdot C_6H_4\cdot CO_2Et,$$

at moderate temperatures and at 125° in a sealed tube has been investigated.

When boiled with alcoholic hydrazine, the ester yields o-*aminosulphonylbenzhydrazide*, $NH_2\cdot SO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH_2$, in very long spikes, m. p. 182°; this forms a *hydrochloride*; a *benzylidene* compound, filamentous needles, m. p. 174°; a m-*nitrobenzylidene* compound, m. p. 215°; and a p-*methoxybenzylidene* compound, pearly flakes, m. p. 184°. The same hydrazide may be obtained by boiling "saccharin" with hydrazine hydrate. When treated with nitrous acid, it is converted into o-*aminosulphonylbenzoylazide*, $NH_2\cdot SO_2\cdot C_6H_4\cdot CO\cdot N_3$, which crystallises in snow-white needles, continually evolves azoimide, detonates at 84°, and is transformed by warming with aniline into *o*-aminosulphonylbenzanilide, m. p. 189°.

If ethyl *o*-aminosulphonylbenzoate is heated with anhydrous hydrazine at 125° in a closed tube and the product is dissolved in hot water, a triazole derivative crystallises on cooling (see below), and the filtrate from this deposits a substituted hydrazine on acidifying with acetic acid. This compound, 2-*hydrazino*-1-*benzsulphonazole* ("*ψ-saccharinhydrazide*"), $C_6H_4<\begin{matrix}SO_2\cdot N \\ \quad\ \ \Vert \\ \text{——}C\cdot NH\cdot NH_2\end{matrix}$, crystallises in very long, silky needles, m. p. 257° (decomp.), dissolves in concentrated hydrochloric acid, but not in dilute, is readily soluble in sodium hydroxide, forming a yellow salt, and reduces ammoniacal silver solutions and Fehling's solution at once in the cold. The same compound may be prepared by heating "saccharin" with hydrazine at 125°, or by mixing hydrazine and 2-ethoxy-1-benzsulphonazole (Jesurun, A., 1893, i, 715). The hydrazine derivative yields a *benzoyl* compound, needles, m. p. 276°, a *benzylidene* compound, m. p. 287°, and an *anisylidene* compound, yellow needles, m. p. 270°. With nitrous acid, it reacts to form 2-*azido*-1-*benzsulphonazole*, needles, m. p. 153° (vigorous decomp.), which may also be prepared by the action of sodium azide on 2-chloro-1-benzsulphonazole (*ibid.*), and reacts with boiling aniline to form 2-*anilino*-1-*benzsulphonazole*,

$$C_6H_4<\begin{matrix}SO_2\cdot N \\ \quad\ \ \Vert \\ \text{——}\cdot C\cdot NHPh\end{matrix},$$

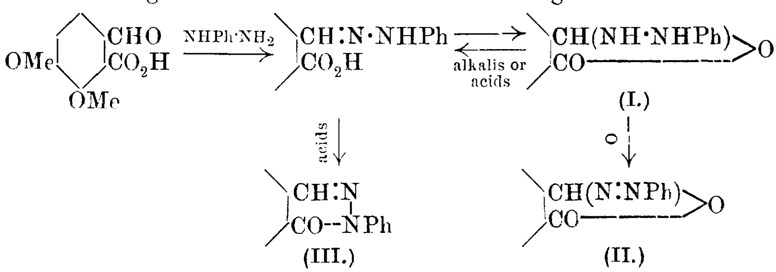
not molten at 300°. The triazole derivative mentioned above is 1-*amino*-2 : 5-*di*-o-*aminosulphonylphenyl*-1 : 3 : 4-*triazole*,

$$\begin{matrix} & N\text{—}NH_2 & \\ & \diagup \quad \diagdown & \\ NH_2\cdot SO_2\cdot C_6H_4\cdot C & & C\cdot C_6H_4\cdot SO_2\cdot NH_2\,; \\ \Vert & & \Vert \\ & N\text{——}N & \end{matrix}$$

it crystallises in stout, glistening, highly refractive prisms, m. p.

242°, and is soluble without decomposition in the concentrated mineral acids. It forms a 1-*benzylideneamino*-compound, m. p. 257°; it is converted by the action of concentrated hydrochloric acid at 180° into 1-*amino*-2:5-*di*-o-*sulphophenyl*-1:3:4-*triazole*, $NH_2{\cdot}N{:}C_2N_2(C_6H_4{\cdot}SO_3H)_2$, prisms, m. p. above 300°, and it loses the 1-amino-group when treated with nitrous acid, yielding 2:5-*di*-o-*aminosulphonylphenyl*-1:3:4-*triazole*, m. p. 286°. J. C. W.

Action of Phenylhydrazine on Opianic, Nitro-opianic, and Phthalonic Acids. Some Derivatives of Hydrazo- and Azo-phthalide. PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN (T., 1917, **111**, 988—993).—Liebermann (A., 1886, 550) found that opianic and nitro-opianic acids react with phenylhydrazine in the presence of acetic acid to form compounds which are insoluble in alkalis, two molecules of water being eliminated. It is now shown that intermediate, soluble products can be obtained if the free base is applied in ethereal solutions, only one molecule of water being eliminated. The new compounds (I) can be oxidised by mercuric oxide to azo-derivatives of a new type (II), or resolved into Liebermann's compounds (III) by means of acetic acid. The various changes are summarised in the following scheme:



Hydrazo- and azo-compounds of the same types have also been obtained from phthalonic acid, but not in a pure state.

For experimental details, see the original. J. C. W.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. III. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, **98**, 89—92. Compare A., 1916, i, 512).—Besides the substances previously described, the author has isolated two other compounds from the products of oxidation of various proteins. One of these is succinic acid and the other α-hydroxy-β-methylpropionic acid. The latter acid probably originates from the α-amino-β-methylpropionic acid, which has been shown to be present in caseinogen (compare Foreman, A., 1913, i, 1249).

H. W. B.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. IV. p-Nitrobenzoic Acid as an Oxidation Product of Proteins. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, **98**, 93—96. Compare A., 1916, i, 512).—Glutin, which contains phenylalanine, but neither tyrosine nor

tryptophan, yields *p*-nitrobenzoic acid when oxidised with nitric acid. This confirms the conclusion drawn by the author that the *p*-nitrobenzoic acid present among the oxidation products of proteins originates exclusively from phenylalanine.

Phenylalanine has not hitherto been detected as a constituent of (i) keratin from horse's hair, (ii) keratin from goose feathers, (iii) spongin, or (iv) ichthyolepidin. On oxidation with nitric acid, however, all these substances yield a small proportion of *p*-nitrobenzoic acid, and therefore each contains phenylalanine.

H. W. B.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. V. Formation of Oxalic Acid from Proteins and Amino-acids. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1916, **98**, 97—115. Compare A., 1916, i, 512).—Glutin and spongin exhibit a marked resistance to nitric acid under conditions in which other proteins are oxidised with formation of 45% of oxalic acid. When fuming acid is employed, oxidation takes place to a certain extent, about 18% of oxalic acid being produced. If, however, about 10% of its weight of cystine, tyrosine, or tryptophan, or a mixture of these amino-acids, is added to glutin, oxidation with ordinary concentrated nitric acid occurs just as with other proteins, and about the usual 45% of oxalic acid is produced. Now glutin does not contain these three particular amino-acids, and, moreover, the removal of these amino-acids from proteins such as fibrin causes the residual amino-acids to become resistant to nitric acid, a resistance which immediately vanishes when one or more of these amino-acids are replaced. Since fuming nitric acid containing free oxides of nitrogen causes oxidation, and it has been shown that cystine, tyrosine, and tryptophan are readily oxidised by nitric acid, with production of oxides of nitrogen, the author draws the conclusion that the presence of these oxides of nitrogen is indispensable for the normal oxidation of proteins with production of the normal quantity (45%) of oxalic acid. The addition of tyrosine, tryptophan, or cystine to spongin likewise ensures its normal oxidation by concentrated nitric acid.

When the nitric acid is allowed to act at 120° instead of at 100°, most amino-acids and proteins are readily oxidised, but only 4—6% of oxalic acid can be recovered from the products of oxidation.

The alleged accelerating action of calcium and magnesium salts in the oxidation of gluten by nitric acid (Sadikoff, A., 1909, i, 750) is not confirmed.

H. W. B.

Comparative Analyses of Fibrin from Different Animals. ROSS AIKEN GORTNER and ALEXANDER J. WUERTZ (*J. Amer. Chem. Soc.*, 1917, **39**, 2239—2242).—Fibrin was prepared from the blood of cattle, sheep, and pigs, and the nitrogen distribution in each sample determined by Van Slyke's method. No differences significantly greater than the probable experimental errors were

found. Thus, apparently, the fibrin from any of these sources can be interchanged in experimental work without vitiating the results.

W. G.

The Crystallisation of Acid Hæmochromogen. CH. DHÉRÉ, L. BAUDOUX, and A. SCHNEIDER (*Compt. rend.*, 1917, **165**, 515—517).—Acid hæmochromogen can be obtained in a crystalline state by heating crystalline hæmin with 60% methyl alcohol and a trace of sodium hyposulphite in a sealed tube at 60—65° for fifteen minutes. At the end of twelve to fourteen hours, acid hæmochromogen is deposited in a crystalline form. The crystals, which are distinctly pleochroic, belong to the rhombic system, the acute angles having a value 84°20′. Complex crystals are sometimes obtained consisting of three simple crystals with their planes perpendicular to one another. W. G.

[Porphyrins.] Valuation of Spectroscopic Methods. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, **98**, 65—72).—Polemical, in reply to Fischer (A., 1916, i, 775), relating to the value to be assigned to spectroscopic methods for the identification of porphyrins and similar compounds. H. W. B.

Constitution of Cotoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, **98**, 14—24. Compare A., i, 575, 775).—It has previously been noted that there are two atoms of oxygen in cotoporphyrin which are not in the form of a carboxyl radicle. Apparently, they are not present as alcoholic hydroxyl groups, such as are found in hæmatoporphyrin, because treatment with dilute hydriodic acid in the presence of phosphorus (which readily reduces hæmatoporphyrin to mesoporphyrin) does not effect any reduction of cotoporphyrin. Probably they are combined directly to carbon atoms in the pyrrole nuclei, similarly to those in bilirubic acid. Energetic treatment with hydriodic acid causes disruption of the molecule and liberation of phonopyrrolecarboxylic acid, unaccompanied by any isomeric pyrrolecarboxylic acid or any recognisable basic fraction.

Oxidation of cotoporphyrin with lead peroxide or with chromic acid yields hæmatic acid, which is identical with that obtained from hæmatoporphyrin. On treatment with potassium methoxide under pressure, the molecule is broken down, and among the products are phyllopyrrolecarboxylic acid and a *substance*, which is possibly a pyrroline derivative.

When methylcotoporphyrin is dissolved in glacial acetic acid and treated with fuming hydrochloric acid and hydrogen peroxide, it is converted into the *dihydrochloride* of *tetrachlorocotoporphyrin*, $C_{36}H_{34}O_8N_4Cl_6$, which crystallises in glittering, prismatic needles. The change is accompanied by complete removal of the methyl groups. Corresponding treatment with hydrobromic acid yields the *dibromide* of *tetrabromotrimethylcotoporphyrin*, $C_{39}H_{40}O_8N_4Br_6$, glittering needles, in which the methyl groups are retained. These

compounds resemble those obtained from mesoporphyrin (compare Fischer and Röse, A., 1913, i, 1006). H. W. B.

Constitution of Urinoporphyrin. Preparation of a Carboxylated Hæmatic Acid from Urinoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, **98**, 78—88. Compare A., 1916, i, 575, 775).—When methylurinoporphyrin is dissolved in a mixture of glacial acetic and hydrochloric acids and treated with hydrogen peroxide, a change in colour from red to green rapidly occurs, and, on the addition of water, *tetrachlorotetramethylurinoporphyrin dihydrochloride*, $C_{47}H_{48}O_{16}N_4Cl_6$, is precipitated in radially-marked, little balls. The solution in chloroform examined spectroscopically shows an absorption band in the red and another in the bluish-violet regions of the spectrum. The formation of this tetrachlorourinoporphyrin indicates that the replaceable hydrogen atoms in urinoporphyrin and cotoporphyrin are similarly situated, and are probably contained in α-methine groups, such as are present in the blood pigments. In accordance with this hypothesis, the carboxyl radicles must be in the β-position, and, by oxidation, a *di-β-carboxylated haematic acid*, $C_9H_9O_6N$, has actually been obtained. The urinoporphyrin is dissolved in 50% sulphuric acid and treated with chromic acid. The oxidation occurs immediately, and the ether extract yields, on evaporation, prisms, m. p. 180—183°, which, after drying over phosphoric oxide, soften, when heated, at 170°, m. p. 188° (decomp.). The compound is identified by heating in a vacuum, when hæmatic acid is formed, which, at 260°, yields methylethylmaleinimide.

Urino- and coto-porphyrins are readily precipitated from a urine containing porphyrins by the addition of acetic acid. They may be separated by dissolving the mixed porphyrins in methyl alcohol saturated with dry hydrogen chloride, and allowing to remain. After twenty-four hours the crystalline hydrochloride of trimethylurinoporphyrin separates out, from which the urinoporphyrin can be readily regenerated in the manner previously described (*loc. cit.*). H. W. B.

Influence of Glycerol on the Activity of Invertase. ÉM. BOURQUELOT (*Compt. rend.*, 1917, **165**, 567—569).—The activity of invertase, as regards the hydrolysis of sucrose, is weakened by the presence of glycerol, the effect increasing with the proportion of glycerol present. W. G.

Physiological Chemistry.

Amount of Dextrose in Blood. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, **98**, 179—180. Compare A., 1916, ii, 454).—The author considers that more accurate information regarding the

amount of dextrose in human blood may be obtained by the application of Oppler's "fractional reduction" method (A., 1912, ii, 100).

H. W. B.

Sugar Absorption and the Pancreas. K. von Körösy (*Zeitsch. physiol. Chem.*, 1916, **98**, 37—48. Compare A., 1913, i, 1128).—Experiments on dogs are described which indicate that when the blood is prevented from circulating through the organs of the body, including the pancreas, the introduction of a large quantity of dextrose solution into the intestine leads to an increase in the amount of dextrose in the blood; whilst if the pancreas is left in the circulation, under otherwise similar conditions, a decrease in the amount of dextrose in the blood is observed. H. W. B.

The Normal Metabolism of the Guinea Pig. L. Millard Smith and Howard B. Lewis (*J. Amer. Chem. Soc.*, 1917, **39**, 2231—2239).—Guinea pigs have been fed on a diet of carrots or cabbage, the urine collected in twenty-four hour periods, and determinations made of the total nitrogen, ammonia, carbamide, creatinine, chlorides, and phosphates in the urine and the hydrogen-ion concentration and total acidity of the urine. The creatinine excretion was found to be constant and independent of the nature or extent of the diet, indicating that uniform daily samples of urine were obtained. The creatinine-coefficient was 12 to 14. The hydrogen-ion concentration of the urine was approximately $P_{H^+} = 8 \cdot 9$ on a carrot diet and $P_{H^+} = 7 \cdot 6$ on a cabbage diet, these differences corresponding with the differences in the composition of the ash of these two vegetables. The elimination of total nitrogen was higher on a cabbage than on a carrot diet, the carbamide nitrogen being a constant proportion (84%) of the total nitrogen. The ammonia content of the urine was negligible. The urinary excretion of phosphorus was greater on a carrot than on a cabbage diet. W. G.

Metabolism of Fats. I. Utilisation of Palmitic Acid, Glyceryl Palmitate, and Ethyl Palmitate by the Dog. J. F. Lyman (*J. Biol. Chem.*, 1917, **32**, 7—11).—In dogs, 95% of ingested glyceryl palmitate is absorbed. The corresponding figures for ethyl palmitate and palmitic acid are 55% and 82% respectively. Ethyl palmitate is not readily hydrolysed in the alimentary canal, and it is probable, therefore, that the absorption and utilisation of the esters of fatty acids are limited by the rate of hydrolysis. The inferior utilisation of the free palmitic acid is due to disturbance of the digestive processes by the irritating action of the free fatty acid on the digestive organs. H. W. B.

Metabolism of Fats. II. Effect of Feeding Free Palmitic Acid, Glyceryl Palmitate, and Ethyl Palmitate on the Depôt Fat in the White Rat. J. F. Lyman (*J. Biol. Chem.*, 1917, **32**, 13—16).—The fat deposited in the adipose tissue of rats after feeding with free palmitic acid, glyceryl palmitate, or ethyl palmi-

tate consists chiefly of tripalmitin in all cases. Appreciable amounts of ethyl palmitate or of palmitic acid could not be detected in the adipose tissue during any of the feeding experiments. These results are in harmony with the hypothesis that hydrolysis of fatty substances occurs before absorption, and afterwards the normal fats are synthesised in the tissues. H. W. B.

Temperature-coefficients of Life Processes. W. J. V. Osterhout (*J. Biol. Chem.*, 1917, **32**, 23—27).—The author points out that life processes consist of a series of consecutive reactions instead of simple chemical reactions (in which the substances formed are not at once broken down), and that change of temperature may affect the former in an entirely different manner from that in which it affects the latter. It is shown, by examples, that in the case of consecutive reactions, if the reaction in which a substance is formed has a different temperature-coefficient from that in which it is destroyed, the type of curve showing the rate of disappearance of the substance may be completely altered by a change in the temperature. Caution must therefore be exercised in interpreting the temperature-coefficients of consecutive reactions, to which category many life processes undoubtedly belong. H. W. B.

Hæmatoporphyria congenita and the Natural Porphyrins. O. Schumm (*Zeitsch. physiol. Chem.*, 1916, **98**, 123—178).—In hæmatoporphyria congenita, the blood contains free hæmatin and a porphyrin. On the addition of acetic acid to the urine, the porphyrin is precipitated, and on spectroscopic examination is found closely to resemble urinoporphyrin (compare Fischer, A., 1916, i, 514; this vol., i, 713). The urine usually contains about 0·02% of porphyrin, whilst the quantity passed daily varies between 0·3 and 0·4 gram.

Comparison of the absorption spectra of urinoporphyrin, cotoporphyrin, hæmatoporphyrin, and mesoporphyrin reveals small differences which indicate that all these porphyrins are distinct compounds. H. W. B.

Porphyrin Occurring in Urine after Trional-poisoning. Alexander Ellinger and Otto Riesser (*Zeitsch. physiol. Chem.*, 1916, **98**, 1—10).—The porphyrin present in the urine after trional poisoning is apparently identical with that discovered by Hans Fischer (A., 1915, i, 514; see also this vol., i, 713) in the urine in a case of congenital hæmatoporphyrinuria, and termed by him urinoporphyrin. It gives the same analytical and spectroscopical data, and shows the same chemical and biological behaviour as urinoporphyrin; the only point of difference observed is in the melting point of the methyl ester, which is found to be 255—257° instead of 290° given by Fischer. The reason for this observed difference could not be discovered. H. W. B.

Production of Cholesterol Esters in Fatty Degeneration. Franz Valentin (*Zeitsch. physiol. Chem.*, 1916, **98**, 73—77).—A portion of degenerated adipose tissue from a pig was observed under

the microscope to contain numerous crystals of two distinct types. Extraction with ether yielded considerable quantities of the fatty acid esters of cholesterol and of free fatty acids; the presence of a lipase in the adipose tissue was also demonstrated. The author suggests that the free fatty acids present in the specimen of adipose tissue represent the products of the action of the lipolytic enzyme, whilst the cholesterol esters have been subsequently synthesised directly from the free acids and cholesterol. H. W. B.

Human Gall Stones. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1916—1917, **98**, 25—36, 281—284).—Human gall stones contain free palmitic acid and a bile acid, which is probably deoxycholic acid.

When a solution of cholesterol in warm butyric acid is cooled, needle crystals appear, which consist of *cholesterol butyrate*. The compound is very easily hydrolysed; on treatment with alcohol, free cholesterol is regenerated. H. W. B.

Behaviour of Dimethylenegluconic Acid and Methylenesaccharic Acid in the Organism. CESARE PADERI (*Arch. Farmacol. sperim.*, 1917, **23**, 353—370; from *Chem. Zentr.*, 1917, ii, 239).—Both acids in the form of their sodium salts are readily tolerated by rabbits. Formaldehyde is not present in the urine which contains the unchanged acids, which must therefore be very stable in the organism. This behaviour is in striking contrast with that of anhydromethylenecitric acid, which is readily hydrolysed with the formation of formaldehyde. The difference is probably due to the fact that, in the former acids, the hydrogen atoms of the methylene group are replaced by two alcoholic hydroxyl groups, whilst in the latter the carboxyl group is also affected. H. W.

Combustion of Benzene in the Human Organism. DIONYS FUCHS and ALAD VON SOÓS (*Zeitsch. physiol. Chem.*, 1916, **98**, 11—13).—The administration of 71 grams of benzene to a man suffering from leucæmia was followed by the elimination of muconic acid in the urine, 0·08 gram of the pure substance being isolated. The oxidation of the benzene nucleus according to the equation $C_6H_6 + 2O_2 = CO_2H\cdot CH{:}CH\cdot CH{:}CH\cdot CO_2H$, occurs, therefore, in man as well as in rabbits and dogs (compare Jaffé, A., 1909, ii, 914). H. W. B.

Toxicity of Aromatic Nitro-compounds. F. KOELSCH (*Münch. med. Woch.*, 1917, **64**, 965—968; from *Chem. Zentr.*, 1917, ii, 309).—The aromatic nitro-compounds have previously been classed in the literature as a group possessing equal toxicity and similar physiological properties. The author gives a series of results obtained by experiments on animals, together with data obtained from the munition industry, and discusses the injury to the health of the workers and the necessary precautions. The following substances are considered: the nitrated benzenes, toluenes, and xylenes, nitronaphthalenes, trinitrotoluene, and the nitrated phenols. The original paper must be consulted for details. H. W.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. II. Emetic Effect and Irritant Action. A. L. WALTERS, C. R. ECKLER, and E. W. KOCH (*J. Pharm. Exper. Ther.*, 1917, **10**, 185—197. Compare Walters and Koch, this vol., i, 612).—In cats, the emetic dose of emetine hydrochloride is approximately twice that of cephaeline hydrochloride, and the higher homologues of the series decrease in emetic power very much in the same ratio as they do in toxicity (*loc. cit.*). The hydrochloride, hydrobromide, and hydriodide of emetine possess about equal emetic power, but the hydriodide of cephaeline *iso*amyl ether, owing to its relative insolubility, is about one-half as emetic as the hydrobromide or hydrochloride of cephaeline *iso*amyl ether, and only one-sixth as emetic as emetine hydrochloride.

When tested on the conjunctiva of rabbits, emetine and cephaeline are the most irritant, and cephaeline *iso*amyl ether is the least irritant of the series. When injected intramuscularly in rabbits, cephaeline *iso*amyl ether is the most irritant, whilst the difference between the other less irritant members of the series is not marked. In man, the hypodermic injection of cephaeline *iso*amyl ether phosphate or hydrochloride causes severe pain, soreness, and local inflammation, whilst with the corresponding propyl ether phosphate, only a slight local reaction is noticeable.

H. W. B.

Fate of Caseinogen after Intravenous Injection. B. VON AÁRON (*Zeitsch. physiol. Chem.*, 1916, **98**, 49—58).—About 58% of the caseinogen administered intravenously to dogs passes unchanged into the urine. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Effects of Alkali Salts on Nitrification. P. E. BROWN and E. B. HITCHCOCK (*Soil Sci.*, 1917, **4**, 207—229).—A study of the effect of applications of sodium chloride, sodium sulphate, magnesium sulphate, and calcium carbonate to normal soil, and of sodium hydrogen carbonate, sodium carbonate, calcium carbonate, and calcium sulphate to an alkali soil, on nitrification in the soil. In the first group, it was found that the toxicity varied with the soil. In the particular soil studied, sodium chloride had a toxic effect at a concentration of 0·02%, sodium sulphate at 2·0%, and calcium carbonate at a point between 1·5 and 6·0%. In the second group, calcium sulphate had no effect, calcium carbonate acted as in the normal soil, whilst sodium carbonate and sodium hydrogen carbonate both had a toxic effect at a concentration of 0·30%. Similar tests in greenhouse soils agreed with these laboratory tests

for alkali soils. In the normal soils, however, in the greenhouse tests the sodium sulphate had a toxic effect at a concentration of 0·5%. The effect of the salts on crop growth was similar to that on nitrification. W. G.

The Nature of Ammonification. K. MIYAKE (*Soil Sci.*, 1917, **4**, 321—325).—A further study of the ammonification of leucine and tyrosine in five different types of soils confirms the statement that this process is an autocatalytic chemical reaction (compare this vol., i, 244). In the case of the two compounds mentioned, it was found that the whole of the nitrogen added was not transformed into ammonia during the process, and that the amount so transformed varied with the nature of the compound added and of the soil to which it was applied. W. G.

Chemistry of Nutrition. TH. BOKORNY (*Arch. Anat. Physiol. Physiol. Abt.*, 1916, 255—294; from *Chem. Zentr.*, 1917, ii, 232).—The number of organic substances which can serve as nutriment for green plants is large and includes the following compounds: For fungi: methyl, ethyl, and propyl alcohols; phenol, glycerol, ethylene glycol, erythritol, mannitol, dulcitol, quinol, tannin, formic, acetic, oxalic, propionic, lactic, succinic, tartaric, butyric, citric, aspartic, glyoxylic, pyruvic, lævulic, salicylic, quinic, benzoic, fumaric, malonic, and malic acids, sucrose, dextrose, lævulose, galactose, lactose, rhamnose, sorbinose, arabinose, maltose, inositol, mannose, xylose, erythrodextrin, salicin, amygdalin, raffinose, dextrin, inulin, cellulose nitrate, cellulose, *p*-hydroxybenzaldehyde, carbamide, glycine, trimethylamine (?), methylamine, propylamine, asparagine, aspartic acid, leucine, tyrosine, toluidine, aniline, creatine, hydantoin, allantoin, peptone, acetoacetic ester, acetone, formaldehyde as methylal, or, less frequently, as sodium formaldehyde sulphite, acetaldehyde, *p*-hydroxybenzaldehyde. For algæ and other green plants: methyl alcohol, ethyl alcohol (?), phenol, glycerol, ethylene glycol, mannitol, dulcitol, acetic, oxalic, propionic, lactic, succinic, tartaric, butyric, valeric, citric, aspartic, glyoxylic and malic acids, sucrose, dextrose, lævulose, galactose, lactose, maltose, formaldehyde, carbamide, glycine, trimethylamine, aspartic acid, leucine, tyrosine, creatine, hydantoin, formaldehyde (free and as methylal or sodium formaldehyde sulphite), peptone, acetoacetic ester. For the full details the original paper must be consulted. H. W.

Action of Radium on Plants in Water Cultures. FERDINAND PILZ (*Zeitsch. Landw. Versuchswesen Oesterreich*, 1916, 399; from *Bied. Zentr.*, 1917, **46**, 412—414).—Experiments were made with the crude residues from the extraction of uranium ore, the radium content of the former being 0·4 mg. per kilo. The material was diluted one hundred times by admixture with pure quartz sand before being employed for the water cultures. Peas and maize were grown in Tollens's solution, which was changed weekly, with the addition of 1 gram of the radium mixture in the earlier stages and

2 grams in the later ones. Thus the set of plants in each culture vessel received 29 grams of the mixture or 0·000116 mg. of radium during the vegetation period. The results show a marked response of the pea plants to the presence of radium, the total dry matter being increased by 28 per cent., whilst the number of pods was increased by 43 per cent. With maize the effect was less pronounced; the total dry matter of the treated plants was 15% higher, but the yield of grain was decreased by 47 per cent. This is attributed to the effect radium has on the retardation of ripening.

Analyses of the plants showed that the percentage of nitrogen, phosphoric acid, potassium, and calcium in the plants grown in the presence of radium is lower than in the controls. The calcium content of the roots is especially reduced, and this effect of decreasing calcification of the root vessels is held to be analogous to the effect of radium on the animal organism. H. B. H.

Seeds of Pangium Edule and of Hydnocarpus Alcalæ. Harvey C. Brill (*Philippine J. Sci.*, 1917, **12**, [*A*], 37—46).—The seeds of *Pangium edule*, a plant found in various parts of the Philippine Islands, are about 5 cm. long by 3 cm. wide, and are embedded in a crustaceous pericarp which is about 22 cm. long by 15 cm. in diameter. They contain a cyanogenetic glucoside, which is identical with gynocardin isolated from *Gynocardia odorata* and the leaves of *Pangium edule* (compare Power, Lees, and Barrowcliff, T., 1905, **87**, 349, 896; De Jong, A., 1909, ii, 424); an enzyme, gynocardase, is also present. The quantity of oil in the dry kernels is 21%. The fruit of *Hydnocarpus alcalae* resembles a small, unhusked coconut and contains numerous seeds about 4 cm. long; the seeds yield 65% of oil. The presence of a cyanogenetic glucoside is doubtful. The two oils have the following physical and chemical characters:

	Pangium edule.	*Hydnocarpus alcalæ.*
M. p.	About 2°.	32°.
D^{30}	0·9049	0·9502
$[\alpha]_D$ in chloroform	+4·28°	+49·60°
n_D	1·4665	1·4770
Iodine number	113·1	93·1
Saponification number	190·3	188·9
Reichert-Meissl number	—	4·43

The oil from *Pangium edule* seeds contains a small quantity of an optically active acid (hydnocarpic or chaulmoogric acid), whilst the oil from *Hydnocarpus alcalae* seeds contains chaulmoogric acid, but not hydnocarpic acid. W. P. S.

Methods for Approximating the Relative Toxicity of Cotton-seed Products. Frank E. Carruth (*J. Biol. Chem.*, 1917, **32**, 87—90).—During the expression of the oil from partly cooked cotton-seed by the hot pressing process, the glands containing the gossypol are disintegrated and the gossypol is spread over the surface of the seed tissue. Apparently, in these circumstances, the

gossypol undergoes oxidation, and is transformed into "D" gossypol, which is much less toxic and less soluble than ordinary gossypol. The toxicity of cotton-seed products is due chiefly to the presence of unchanged gossypol, which may be detected in the following ways: (1) a portion of the meal is sprinkled on a glass slide and touched with a drop of concentrated sulphuric acid. The result is observed immediately through the low power of a microscope. In the presence of unchanged gossypol, numerous red areas appear where the acid touches the more or less disintegrated glands; (ii) about 200 grams of the meal are extracted with ether. The extract is concentrated, filtered, and treated with about one-tenth of its weight of aniline. After warming on the water-bath, the mixture is left for several days. The more gossypol there is present, the quicker will be the appearance of a yellow, microcrystalline precipitate of the *dianiline* salt of gossypol, $C_{30}H_{28}O_9,2C_6H_5{\cdot}NH_2$, which can be collected on a tared Gooch crucible, washed with ether and light petroleum, dried at 100°, and weighed.

Cotton-seed meal which has been cooked for twenty to thirty minutes during the pressing process may be practically free from toxic properties, and the ethereal extract treated in the manner described above fails to give any precipitate with aniline.

The meal prepared by the cold pressing process may not be more toxic than the hot pressed meal. It appears that most of the gossypol passes in the former process into the oil, from whence it is subsequently entirely removed during the process of refining.

H. W. B.

[Oxalic Acid in Foods.] E. Arberg (*Mitt. Lebensmittelunters. Hygiene*, **8**, 98—104; from *Chem. Zentr.*, 1917, ii, 320—321).—See this vol., ii, 583.

Occurrence of Manganese in Insect Flowers and Insect Flower Stems. C. C. McDonnell and R. C. Roark (*J. Agric. Research*, 1917, **11**, 77—82).—The authors have determined the amounts of manganese present in the stems, "open" flowers, and "closed" flowers of *Chrysanthemum cinerariaefolium* from Japan and from Dalmatia, and find that the manganese content of both stems and flowers vary considerably and is but little different in the two parts of the plant. The estimation of the manganese content of an insect powder in order to detect adulteration with powdered stems is therefore useless. Pyrethrum of Japanese origin contains more manganese than that from other countries, probably owing to the high manganese content of the volcanic soils of Japan. The manganese, nitrogen, and phosphoric acid content of pyrethrum vary in the same direction. W. G.

The Diastatic Degradation of Inulin in Chicory Root. J. Wolff and B. Geslin (*Compt. rend.*, 1917, **165**, 651—653).—Inulin breaks down in the chicory root under the influence of enzyme action to lævulose with the intermediate formation of compounds which the authors call inulides, these being capable of con-

version into lævulose by the hydrolytic action of the juice itself. They are also fermented by different yeasts, but vary in their resistance to this action. The fresh juice of the chicory, although capable of hydrolysing these inulides, is without action on pure inulin.

W. G.

Preparation of Durable Fruit Extracts, which contain the Fragrant Substances and Enzymes of the Fruit Juices in an Undecomposed Form. H. Thoms (*Ber.*, 1917, **50**, 1240—1242; D.R.-P., 285304, June, 1914).—The fruit juices are dialysed (for apparatus, see this vol., ii, 561), and so freed from most of their dissolved acids, and then evaporated to syrups in vacuum pans at below 40°. The extracts thus contain the undecomposed enzymes, but are durable. A pineapple syrup is described which contained about 3·5% of valuable proteolytic enzymes.

J. C. W.

Effect of Three Annual Applications of Boron on Wheat. F. C. Cook and J. B. Wilson (*J. Agric. Research*, 1917, **10**, 591—597).—The boron was used in the form of borax or colemanite as a fly larvicide for horse manure, which was then applied to the soil. Four plots were used: (1) unmanured, (2) manured control, (3) manured plus borax, (4) manured plus colemanite. The amount of borax applied in the first year was equivalent to 0·0088% boric acid to the top 0·15 metre of soil and 0·0022% in the two subsequent years. The amount of colemanite applied was equivalent to 0·0029% boric acid to the top 0·15 metre of soil each year. In the first two years the borax reduced the yield of grain by 10% against the manured control, while the colemanite had little, if any, effect. In the last year, when the yields from all four plots were low and the proportion of straw to grain was high, the borax plot gave the best yield. Only minute amounts of boron were absorbed by any of the wheat plants, and in all cases a relatively uniform distribution of boron in the straw and grain was found. Only in the first year on the borax plot was a yellowing of the plants observed, and a sample of soil from this plot taken nine months later showed the presence of boron soluble in weak acid. In no other soil sample was any soluble boron found. There was no evidence of any cumulative action of boron in the soil. W. G.

The Occurrence of *l*-Leucine in Sweet Clover Silage. G. P. Plaisance (*J. Amer. Chem. Soc.*, 1917, **39**, 2087—2088).—Although mannitol is readily isolated from silage made from maize, cane and sunflower (Dox and Plaisance, this vol., i, 683), sweet clover silage yields no trace of mannitol, but extraction with alcohol in this case yields *l*-leucine in quantity corresponding with 0·4 to 1% of the dry material. No sample of maize silage has been found to contain *l*-leucine. D. F. T.

Effect of Paraffin on the Accumulation of Ammonia and Nitrates in the Soil. P. L. Gainey (*J. Agric. Research*, 1917, **10**, 355—364).—The unsatisfactory results obtained by the "paraffin

wire-basket method" of studying soil fertility (compare Gardner, U.S. Dept. Agric. Bur. Soils, Circ. 18) are shown to be due to the growth of certain saphrophytic fungi, which is encouraged by the paraffin either in the form of wax or oil. This development of fungi is accompanied by the disappearance of active ammonia or nitrate nitrogen. Very similar results are obtained whether the bottle containing the soil is simply coated on the inside with paraffin wax, or chips of the wax or paraffin oil are incorporated with the soil. When nitrogen is added to the soil in the form of cotton-seed meal, vigorous ammonia and nitrate formation occurs, but the nitrogen in these two forms rapidly disappears owing to the action of the fungi. W. G.

Some Factors Affecting Nitrate-Nitrogen Accumulation in Soil. P. L. GAINEY and L. F. METZLER (*J. Agric. Research*, 1917, **11**, 43—64).—A study of the effects of varying the depth of the column of soil, its moisture content, and compactness on nitrate accumulation. The experiments were carried out in the laboratory on a silt loam. The results indicate that as the moisture content of a soil decreases, increasing the compactness from a very loose condition will increase the accumulation of nitrate nitrogen. The optimum moisture content for any degree of compactness is such that the soil contains about two-thirds of the total amount of moisture it will retain. When this condition is fulfilled, aeration will be sufficient to the depth of 3 decimetres with any degree of compactness, and it is further found that the accumulation of nitrate nitrogen increases with increasing depth down to 6 decimetres. Nitrate nitrogen accumulates more rapidly in unbroken soil columns than in artificial columns of powdered, sieved soil. Aeration in a column of soil uncultivated for seven years was found to be far in excess of that required to maintain aerobic conditions. W. G.

Absorption and Nitrification of Ammonium Compounds in the Presence of Zeolites in Soil. Estimation of Ammonia in Soil and on Zeolithic Substances. F. MÜNTER (*Landw. Versuchs. Stat.*, 1917, **90**, 147—189).—Sandy soil possesses an appreciable capacity of absorbing ammonia from ammonium sulphate. A portion of this absorbed ammonia can be recovered by distillation with magnesia, but upwards of 10% is more firmly retained. By the addition of zeolites, the amount absorbed may be increased by a further 20—25% of the total added. It is found that the ammonia held by sandy soil is more easily nitrified than that held by zeolites. Soil and zeolite react similarly in retaining some ammonia when boiled with magnesia, but whilst that held by the latter can be completely recovered by a further addition of potassium chloride before distillation, some of that retained by the soil is much more resistant to treatment. Pure sand is unable to absorb ammonia, and the addition of silicic acid and aluminium hydroxide is without effect.

Experiments were made on the estimation of ammonia in soils,

and the result obtained that the hydroxides and carbonates of calcium, barium, strontium, and sodium, with or without the addition of neutral salts, either fail to expel all the absorbed ammonia or else lead to decomposition of the soil organic matter. The general conclusion is drawn that adsorption and absorption occur simultaneously in the soil without any definite relation existing between the two. H. B. H.

An Agronomic Study of several Fertilising or Anticryptogamic Compounds Used in Agriculture. Bogumil de Wilkoszewski (*Arch. Sci. phys. nat.*, 1917, [iv], **44**, 165—189, 256—275).—Solutions of various salts have been allowed to percolate through columns of natural and artificial soils of different types and the water draining through examined. Iron in solution as ferric sulphate is more rapidly absorbed by the soil than in the ferrous state, any iron retained from ferrous sulphate being found in the ferric state in the soil. The salts are converted into their hydroxides, the ferrous hydroxide being subsequently oxidised and held in the soil in the ferric state. This hydrolysis is markedly favoured by the presence of the soil particles. Similar results were obtained with manganese sulphate and copper sulphate, the salt in all cases undergoing hydrolysis, and, where possible, oxidation, the base being retained in the soil and the acid ion passing on into the drainage water.

In the case of calcium cyanamide, this material is converted into carbamide, ammonium carbonate, and subsequently calcium nitrite and nitrate, the reaction being much more rapid where a solution is used than when the solid is itself mixed into the soil. The author considers that micro-organisms are not essential for these changes, as they occurred in a sterilised soil. The oxidation to nitrite and nitrate goes on most rapidly in soils of a porous nature, such as the infusorial earths. The author finds that, in the presence of calcium cyanamide, Nessler's reagent does not give the red precipitate with ammonium salts. W. G.

The Divergent Effects of Lime and Magnesia on the Conservation of Soil Sulphur. W. H. MacIntire, L. G. Willis, and W. A. Holding (*Soil Sci.*, 1917, **4**, 231—237).—Calcium oxide, magnesium oxide, precipitated calcium carbonate, precipitated magnesium carbonate, ground limestone, ground dolomite, and ground magnesite respectively were mixed in with a sandy loam at rates corresponding with 19, 79, and 247 tonnes of calcium oxide per hectare. The samples of soil were then placed in lysimeters either directly on a sand filter bed or having an intermediate 0·3 metre of clay subsoil. The soils were leached by rain and the total alkalinity of, and sulphur in the drainage waters, for two successive years determined. The interposition of the subsoil checked the loss of sulphur by drainage except in the second year after the application of magnesium oxide and magnesium carbonate. The 19-tonne application of calcium oxide slightly depressed the

sulphur in the drainage waters as compared with the other equivalent dressings, but the 79-tonne and 247-tonne treatments practically inhibited the outward movement of sulphur in solution. All the natural carbonates appeared to bring about conditions causing an increased washing out of sulphur as compared with subsoil tanks receiving no application of carbonate. W. G.

Formation of "Black Alkali" (Sodium Carbonate) in Calcareous Soils. J. F. Breazeale (*J. Agric. Research*, 1917, **10**, 541—590).—The formation of sodium carbonate by the action of calcium carbonate on aqueous solutions of sodium nitrate, chloride, or sulphate may be checked, and even prevented, by the presence of relatively small amounts of calcium nitrate or chloride, but a saturated solution of calcium sulphate does not entirely stop the formation of sodium carbonate. In the presence of carbon dioxide, it is sodium hydrogen carbonate which is formed, and the soluble calcium salts have the same effects as in the first case. Thus a field application of gypsum will not overcome "black alkali" if the soil or the irrigation water contains soluble sulphates in appreciable amounts, this formation of sodium carbonate in the soil by interaction of the calcium carbonate and sodium salts proceeding as in aqueous solutions. The sodium carbonate thus formed decomposes the organic matter of the soil, giving very toxic compounds, which may be the cause of the barren or "slick" spots in calcareous soils. The decomposition of the organic matter by the sodium carbonate is checked to some extent by the presence of sodium chloride or sodium sulphate.

A calcareous hardpan may produce "black alkali" by interaction with soluble sodium salts washed down from the upper layers of the soil or brought up from below in the soil water by capillary action. W. G.

The Isolation from Peat of certain Nucleic Acid Derivatives. W. B. Bottomley (*Proc. Roy. Soc.*, 1917, [*B*], **90**, 39—44).—Extraction of air-dried, raw peat with a 1% solution of sodium hydrogen carbonate, the extract being filtered, neutralised with hydrochloric acid, concentrated in a vacuum to a small volume, and then poured into alcohol containing sodium acetate and hydrochloric acid, did not give nucleic acid. The precipitate when examined by Jones's method of hydrolysis was found to contain the dinucleotide, adenine-uracil-dinucleotide, whilst the filtrate contained phosphoric acid, sugar, guanine, and cytosine, the four radicles of a guanine-cytosine-dinucleotide. The nucleic acid in peat is thus apparently split up during peat formation in the same manner as that found for yeast-nucleic acid by Jones and Germann (compare A., 1916, i, 515). W. G.

JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Arc Spectra of Yttrium, Erbium, and their Intermediate Fractions. JOSEF MARIA EDER (*Chem. Zentr.*, 1916, ii, 455—456; from *Sitzungsber. K. Akad. Wiss. Wien. Mathem. naturw. Kl.*, [11 *A*], **125**).—The author has redetermined the spectrum of yttrium, using a very pure specimen of yttrium sulphate; the measurements cover the weaker γ-lines from λ 7881—2231. The emission spectrum of yttrium in the electric flame arc is a mixture of three spectra—a well-defined, strong line spectrum and two types of band spectra. The most characteristic form of the latter consists of groups of regular bands the heads of which are rough and shaded towards the red; these are resolved at great dispersion into a system of groups of very fine lines. In addition to these bands, there is also a weak band spectrum composed of indistinct lines, which only appears after protracted illumination, and in consequence of its indistinctness could not be measured.

The yttrium line spectrum between λ 7881 and 2231 contains 706 lines, the wave-lengths of which are given in tables. The yttrium sulphate was free from erbium and thulium, but contained traces of aldebaranium and holmium. In the band spectrum of yttrium, the first group (α) extends from λ 6338—6132, the second (β) from λ 6137—5972; the third group (γ) is less defined, the most marked band head occurring at λ 5956. The groups of bands

of shorter wave-length are weaker and less definite, and their structure is less regular than that of the α-, β-, and γ-groups. In the region λ 6338—5838, the author finds 20 lines of the yttrium line spectrum and about 700 line components of the yttrium band spectrum.

The arc spectrum of erbium in the region λ 6880—4471 has been measured afresh; the author finds 1780 lines against 800 previously recorded. The results obtained with different preparations of erbium are so discordant that it appears doubtful if the specimens obtained up to the present are sufficiently uniform. The investigation of erbium preparations from the fractions lying towards the thulium groups shows them to contain in all probability the new element dubhium, in addition to thulium and denebium; only minute amounts of yttrium are present. In the arc spectrum of erbium fractions closely related to yttrium, all the brighter yttrium lines are present accompanied by very large numbers of erbium lines, whilst the lines of the thulium group are not so marked. An erbium fraction containing much yttrium yielded a line spectrum in the electric arc between carbon poles in which 4045 lines were measured between λ 6492 and 2326. In addition to a number of holmium lines, this spectrum contained many unidentifiable lines, which point to the presence of a new element (erbium III). The spectroscopic investigation of erbium preparations containing yttrium gave indications of a fission of holmium.

H. W.

The Quantitative Absorption of Light by Simple Inorganic Substances. I. The Haloids of the Alkali Metals and Hydrogen. PETER JOSEPH BRANNIGAN and ALEXANDER KILLEN MACBETH (T., 1916, **109**, 1277—1286).—The curves obtained by plotting the molecular extinction coefficient against the frequency of the incident light show that the haloids of hydrogen and the alkali metals are not diactinic, but exhibit well-marked selective absorption. For a given halogen, the position of the band is independent of the electropositive element or group, the selective frequencies for the chlorides, bromides, and iodides being $1/\lambda = 3730$, 3570, and 2803 respectively. The frequency thus decreases as the atomic weight of the halogen increases.

The curves for the chlorides and iodides show that the extinction coefficient increases with increase in the atomic weight of the positive radicle, but lithium is an exception to this rule.

In seeking for an explanation of the selective effects, chlorine gas was examined, and found to exhibit strong absorption with a minimum at $1/\lambda = 3060$. Halogen-substituted organic compounds give only slight general absorption. These results seemed to show that the selective effects are due to the halogen ions. Since, however, the molecular extinction of the alkali haloids increases with increasing concentration of the solution, it would appear that the bands are not due to the free ions themselves, but are the result of vibrations set up in them under the influence of the positive ion.

The fluorides examined showed no selective absorption, and it is

suggested that the characteristic frequency lies outside the range of ultra-violet rays examined. H. M. D.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXI. The Relationship of the Rotatory Powers of Ethyl Tartrate, *iso*Butyl Tartrate, and *iso*Butyl Diacetyltartrate. THOMAS STEWART PATTERSON (T., 1916, **109**, 1139—1175).—In continuation of previous work (T., 1913, **103**, 145), which was considered to show that in the temperature–rotation curves of ethyl tartrate beyond the maximum actually demonstrated there should be a minimum rotation of positive, but not high value, the rotations of homogeneous ethyl tartrate, homogeneous *iso*butyl tartrate, and homogeneous *iso*butyl diacetyltartrate, and of these esters in solution in a number of solvents, have been examined for light of six or more colours. Salicylaldehyde, benzaldehyde, pyridine, and quinoline tend to displace the maximum rotation in ethyl tartrate towards a lower temperature and a higher rotation value in the sequence given, the first-mentioned solvent being least powerful. In the last three solvents the curves are obviously tending towards minimum values at high temperatures, this minimum being actually reached in the case of quinoline. It might perhaps be that, since the curves for different colours of light in the case of ethyl tartrate intersect before the maximum, they ought again to intersect after the maximum is passed and before the minimum is reached, in which case a region of visibly anomalous rotation–dispersion might be expected at a fairly high temperature. This, however, is not observed. It is shown that the region of visibly anomalous rotation–dispersion for *iso*butyl tartrate is brought into view by solution of the ester in *s*-tetrachloroethane, this region being, therefore, moved towards a higher temperature and a lower rotation value. In quinoline, the behaviour is very much the same as that of ethyl tartrate. Since the solutions in quinoline darken at temperatures just above 100°, the observations cannot be carried far beyond the minimum values, so, to ascertain what happens beyond this minimum value, the behaviour of *iso*butyl diacetyltartrate in the homogeneous condition was examined. A minimum is found in the graphs for this ester at the ordinary temperature, and since at the minimum the rotation–dispersion is positive, thus corresponding quite closely with what is observed in the neighbourhood of the minimum for ethyl tartrate and *iso*butyl tartrate in quinoline, it is concluded that these minima represent corresponding conditions of the substances, so that the behaviour of *iso*butyl diacetyltartrate between, say, 0° and 200° may be held to represent the behaviour of ethyl tartrate or *iso*butyl tartrate at temperatures from perhaps 300° up to about 500°. On heating *iso*butyl diacetyltartrate beyond the minimum, no further intersection of the graphs takes place; no further region of visibly anomalous rotation-dispersion has been observed. By piecing together the evidence referred to, the author concludes that if these three esters were examined over a wide range they would all show, at low temperatures, negative values of

rotation with negative dispersion. As the temperature increased, the temperature–rotation graphs would intersect, giving rise to visibly anomalous rotation–dispersion, continuing to rise to reach maxima at slightly different temperatures. They would then fall again to reach, without further intersection, minimum values, rising thereafter, again without intersection, to attain to new maxima, up to which, in the meantime, they have not been followed. The curves for *iso*butyl diacetyltartrate in *o*-nitrotoluene were found to be remarkable, inasmuch as they exhibit anomalous rotation–dispersion, from which the conclusion is drawn that the effect of this solvent is to displace the minimum of the *iso*butyl diacetyltartrate towards high temperatures, over the maximum corresponding with that actually existing in ethyl tartrate, so as to bring into view the region of anomalous rotation–dispersion corresponding with that which actually exists in ethyl tartrate at the ordinary temperature. It is pointed out that whereas the value of the maximum may be very different, and occur at very different temperatures for a given homogeneous substance and for that substance in solution, or for a derivative of that substance, the rotation value at which the intersection of the temperature–rotation curves for two different colours of light takes place is almost identical. This point is the same as the point of intersection of the two corresponding lines on Armstrong and Walker's characteristic diagram. T. S. PA.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXII. Rotation Dispersion. THOMAS STEWART PATTERSON (T., 1916, **109**, 1176—1203).—Since, as is shown, the ordinary rotation–dispersion ratios may vary for quite slight changes of external conditions, such as temperature, between +infinity and −infinity, they have obviously very little value. If, however, the dispersion ratio be calculated with respect to the intersection of the corresponding temperature–rotation curves or the intersection of the corresponding lines on Armstrong and Walker's characteristic diagram, this point being regarded as a rational zero for these colours, it is found that the dispersion ratio then shows a very fair constancy throughout a related series of active compounds or for a particular active compound in different solvents or at different temperatures. This is illustrated from data given by Pope and Winmill for benzoyl and various substituted benzoyl, sulphonyl, and naphthoyl derivatives of *l*-tetrahydroquinaldine; by data given by Pickard and Kenyon for methyl-*tert.*-butylcarbinol and *d*-1-naphthyl-*n*-hexylcarbinol, as well as from data from the preceding paper. The manner in which rotation data are likely to lie upon a characteristic diagram in the neighbourhood of a maximum or a minimum in the temperature–rotation curves is discussed. In such cases it appears that the points on the characteristic diagram must return on themselves, whence it seems probable that the data for a given substance should fit approximately on different characteristic diagrams according to the temperature or nature of the solvent. T. S. PA.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXIII. Anomalous Rotation-Dispersion and Dynamic Isomerism. THOMAS STEWART PATTERSON (T., 1916, **109**, 1204—1228).—The hypothesis of Arndtsen, which has recently been revived by Armstrong and Walker, that anomalous rotation-dispersion is due to the presence of two modifications of one original active compound, is discussed, especially with reference to the assumptions which have to be made to account for the occurrence of these isomerides. The contention of Lowry and Dickson, that ethyl tartrate can be separated by distillation into fractions containing active substances of dissimilar constitution, is held not to be justified by the evidence adduced. It is maintained that if in any case solvent influence on rotation can be shown to exist where mutarotation is equally definitely shown to be absent, Armstrong and Walker's theory may, in general, be regarded as disproved. Now the initial rotation of a mutarotatory compound in solution, such as lævulose, is a datum independent of any consideration regarding mutarotation, and if the initial rotation for such a substance in different solvents be different, it is considered that solvent influence exists independently of dynamic isomerism, and that, therefore, the two phenomena are not necessarily connected. An examination of the mutarotation curves for lævulose in water, in water and ethyl alcohol, and in water and pyridine shows that any solvent effect revealed by the initial rotations is less than the errors of observation of the method. Solvent influences of this kind have, however, been detected by Mackenzie and Ghosh (A., 1915, ii, 301), and others, much more definite, by Lowry, for α-nitrocamphor in various solvents, whence it is concluded that this compound shows a decided solvent influence which has nothing to do with dynamic isomerism, whilst it is also clear from Lowry's data that α-nitrocamphor exhibits a concentration effect as well, thus coming into line with ethyl tartrate. It is also pointed out that it would be very difficult to explain the maxima or minima which are often found in the temperature-rotation curves for active substances, on the assumption that the changes in rotation are due to a variation in the proportions of two dynamic isomerides, one with a high rotation and the other with a low rotation. T. S. PA.

A Thermostat for Polarimetric [Determinations] particularly during Sugar Inversion at High Temperatures. THEODOR PAUL (*Zeitsch. physikal. Chem.*, 1916, **91**, 745—755).—A thermostat is described which may be used in connexion with a polarimeter in determining the amount of inversion of sucrose at high temperatures. The main point about the thermostat is that it allows the observation tube, which is made of quartz, to lie horizontally. For mechanical details of both thermostat and observation tube the original must be consulted. The instrument permits of measurements being made at 100°. J. F. S.

Action of Light on the Formation and Decomposition of the Hydrogen Halogen Acids. ALFRED COEHN and KARL STUCKARDT (*Zeitsch. physikal. Chem.*, 1916, **91**, 722—744).—The

authors have investigated the action of light on the gaseous systems hydrogen iodide, hydrogen bromide, hydrogen chloride, and their components. The reactions have been effected by means of a mercury lamp in both quartz and uviol glass apparatus. In all three cases equilibrium has been reached from both sides. In quartz apparatus the decomposition proceeds to the extent of 92·3% in the case of hydrogen iodide, and this is reached in ten minutes; the formation proceeds to 7·6%. In both uviol glass and ordinary glass there is a decomposition of 100% and no formation in the case of hydrogen iodide. With hydrogen bromide there is 100% decomposition in quartz, 20% in uviol glass, and no decomposition in glass. The amount of formation of hydrogen bromide is zero in quartz, 80% in uviol glass, and 100% in glass. In the case of hydrogen chloride there is 0·42% decomposition and 99·58% formation in quartz and 100% formation with no decomposition in uviol glass and ordinary glass. In the case of hydrogen bromide the reaction is complete in four hours and with hydrogen chloride in less than five minutes. The use of the three types of apparatus shows the effect of the different spectral regions in quartz, light down to 220 $\mu\mu$ is active, in uviol glass to 254 $\mu\mu$, and in Jena glass down to 300 $\mu\mu$. The absorption of ultra-violet light by the halogen haloids and the halogens has been determined for various thicknesses of gas. J. F. S.

The Flame Arc in Chemical Manufacture. W. R. Mott and C. W. Bedford (*J. Ind. Eng. Chem.*, 1916, **8**, 1029—1035).—The flame arc at high amperage is, in proportion to the current used, the most efficient source of light known for photo-chemical reactions. The chemical action of the white flame arc through glass on sensitised paper or on *p*-phenylenediamine is three times greater than is that of other coloured flame carbons under similar conditions. The direct-current white flame arc has an action on sensitised paper which can be expressed approximately by the empirical equation: $KC^{1\cdot 8}(V-23)$, where C is the current, V arc voltage, and K a constant having a value of 0·0085. The white flame arc is better suited for use with glass vessels than with quartz vessels; at high arc voltages the light and chemical effect increase as the arc voltage is raised, but at a decreasing rate. The use of the white flame arc opens up many new possibilities for controlling and changing chemical reactions (chlorination, bromination, etc.). A means of using an enclosed arc lamp with flame carbons consists in using a shunt around the lamp resistance and solenoid on a direct current, or a reactance coil in shunt around the lamp reactance coil and solenoid on an alterating current. W. P. S.

The Influence of different Gases on the Photoelectricity of Potassium. G. Wiedmann (*Ber. Deut. physikal Ges.*, 1916, **18**, 333—338. Compare A., 1916, ii, 508).—Previous experiments have shown that the photoelectric sensitiveness of potassium is very greatly diminished and the selective photoelectric effect caused to disappear when the metal is freed from gases by repeated distilla-

tion in a vacuum. The further investigation of the influence of different gases on such purified potassium indicates that argon and nitrogen produce little change in the sensitiveness of the potassium. Oxygen increases it to a small extent, whilst hydrogen is exceedingly active, and there is no doubt that the photoelectricity of ordinary potassium is almost entirely due to the presence of hydrogen in the metal. This gas appears to be responsible also for the selective effect at $\lambda = 436\ \mu\mu$. H. M. D.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. V. Investigations on the Use of the Vreeland Oscillator and other sources of Current for Conductivity Measurements. W. A. TAYLOR and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2396—2403. Compare A., 1915, ii, 406).—The authors have examined a number of instruments for producing alternating currents with the object of ascertaining which is most suitable for use in the measurement of the electrical conductivity of solutions. Experiments have been carried out with an induction coil, the 60-cycle city supply (Madison), a Holzer–Cabot wireless alternating current generator, a General Electric type of large generator, a Siemen's–Halske alternating current generator, a Vreeland oscillator working at 500 and 1000 cycles, and the *B* Vreeland oscillator, which works at from 160 to 4200 cycles. Oscillograms of the voltage wave of the current produced in each case have been prepared, and are reproduced in the paper. The authors find that the Vreeland oscillator is the best and most convenient form of instrument for producing alternating current for the present purpose. It is nearly noiseless in action, and gives practically a pure sine voltage wave; it gives a constant frequency which is independent of the variations in the actuating direct current, and it allows of the frequency being changed to anything which may be desired in conductivity work.

J. F. S.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. VI. Investigations on Bridge Methods, Resistances, Cells, Capacities, Inductances, Phase Relations, Precision of Measurements, and a Comparison of the Resistances obtained by the use of Inductance and Capacity Bridges. W. A. TAYLOR and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2403—2415. See preceding abstract).—A general investigation and discussion on the various factors which affect conductivity determinations of solutions. It is found that the Vreeland oscillator is the most convenient and suitable instrument for producing the alternating current. Curtis coils on porcelain spools should be used for resistances above 10 ohms to prevent errors due to inductance and capacity effects. For the greatest accuracy in balancing a bridge a telephone should be used which can be tuned to any desired frequency and can be attached to a stethoscope. A substitution method as suggested by Curtis for measuring resistance is advantageous, since, by simply regulating

the temperature of the variable resistance it prevents errors due to changes in the resistances of the bridge coils, or in the inductance, caused by variations in temperature, and allows of the direct reading of the resistances instead of having to make involved calculations. The constant temperature-bath and the bridge should be earthed to avoid capacity errors. In order to prevent changes in the resistance of the solutions during measurements, the cells should be made with ground-glass joints, which should be below the surface of the thermostat liquid. The electrodes of the cells should be supported by several glass arms to prevent them changing their position, and the leads to the electrodes should be sealed off in glass tubes, so that they may be kept clean, and changes in resistance thus avoided. Solutions should be made up and analysed by weight methods in resistance glass or quartz vessels, and transferred to the conductivity cell under the water of the thermostat. Resistance measurements on a given solution in a given cell can be reproduced to within 0·001%. Resistance measurements on different parts of the same solution in the same cell agree to within 0·01%, even when no precautions are taken in filling the cell. The resistances of aqueous solutions in cells with platinised electrodes do not change appreciably on keeping in the cell for twenty-four hours. Cells with bright electrodes showed changes in resistance of 0·05—0·14% in twenty-four hours. A comparison of the resistances obtained by the use of (1) an inductance, and (2) a condenser to balance the capacity of a cell, shows that the values of the resistances obtained by the two methods are practically the same, the variation being only ±0·001%. J. F. S.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. VII. Investigations on the True and Apparent Resistances, Voltage, Apparent Capacity, Size and Character of Electrodes, Ratio of Inductance Changes to Resistance Changes, and the Relation of Induction and Capacity to Frequency. W. A. TAYLOR and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2415—2430. See preceding abstracts).—A further paper on the investigation of the various factors which affect the electrical conductivity measurements of solutions. It is shown that there is no measurable change in the resistance of a solution, or the inductance with change in voltage, provided that the cells, solutions, and containers are kept scrupulously clean. If the cells are not clean, however, there is a change in resistance with change of voltage, and this fact may be used as a trustworthy test of the cleanliness of cells. To make accurate conductivity measurements, the cells and methods must be so chosen that the ratios of the resistances for a given solution in two cells, or of two solutions in any cell, are constant to within 0·01%. To achieve this result, electrode effects must be entirely eliminated. From the fact that the ratios of the resistances of *N*/2-, *N*/10-, and *N*/20-solutions of sodium chloride, when measured in cells with 0·5 and 1·0 inch platinised electrodes respectively, did not vary more than 0·01%,

which is the experimental error due to all causes, and since there is no measurable change in the resistance of a solution with a change of frequency from 500 to 2000 cycles with platinised electrodes of more than 1 inch in diameter, it follows that 1 inch platinised electrodes give approximately the true electrical resistances of these solutions at the above-mentioned frequencies, and they certainly do at infinite frequencies if the resistance is above 100 ohms.

In cells with bright electrodes there is a change in resistance with change of frequency from 600 to 1000 cycles and higher. This change depends on several factors: (1) As the concentration of any given solution is decreased, and therefore the resistance increased, the change of resistance with change of frequency is decreased. (2) As the area of the electrode surface is increased, the change in resistance with change in frequency is decreased. (3) As the area of the electrode surface is increased, the inductance necessary to obtain a balance is decreased, and hence the apparent capacity of the cell is increased. (4) The higher the apparent capacity of the cell, and therefore the smaller the inductance necessary to balance this capacity, the smaller the change of resistance with change of frequency becomes. Since the apparent capacity of a cell is increased by increasing the electrode surface, platinised electrodes should give the smallest change in resistance with change of frequency, and this is confirmed by the authors' experiments. (5) Solutions of different salts having about the same resistance in the same cell with bright electrodes give approximately the same change in resistance with change in frequency from 600 to 1000 cycles. (6) There is a specific relation between the electrolyte, the electrode material, the character of the electrode surface, and the change of capacity and resistance with change of frequency. This is shown by the fact that for a change of frequency from 600 to 1000 cycles, $N/10$-silver nitrate in a cell with 1 inch bright platinum electrodes gives a change of 0·12%, a similar solution in the same cell with 1 inch rough, silver-plated electrodes gives a change of 0·012%, and a $N/10$-sodium chloride solution in the same cell gives a change of 0·052%. By comparing the resistances of $N/10$- and $N/20$-solutions of sodium chloride in two cells, one of which had bright and the other platinised electrodes 1 inch in diameter, it is shown that the ratio for the cell with bright electrodes is much lower at the lower frequencies than that for the cell with platinised electrodes, but as the frequency is increased, the ratio for the cell with bright electrodes approached that for the cell with platinised electrodes. On extrapolating the resistance for the cell with bright electrodes to infinite frequency, the ratio was found to differ by only 0·004% from that given by the cell with platinised electrodes. This indicates that the true electrical conductivity of solutions can be measured in cells with bright platinum electrodes only at infinite frequency. It is therefore recommended that for conductivity work involving an accuracy of 0·01% a Vreeland oscillator, giving frequencies of 500, 750, 1000, and 1500 cycles, be used, and

the corresponding resistances be extrapolated to give that at infinite frequency.

By substitution in the equation $(R_f - R_{f\infty})/L_f f = K$, in which R_f and L_f respectively are the resistance and inductance measurements at a given frequency f, R_∞ is the resistance at infinite frequency, and K a constant, it is possible to calculate R_∞ for any given cell and solution. The values found for R_∞ by this equation differ from those found by extrapolation by only ±0·01% to ±0·025%. It is recommended, since there is a change of resistance with frequency, that all conductivity and resistance measurements should be given at infinite frequency. Saturation of electrodes with hydrogen produces no appreciable change in the capacity of a cell at 60 cycles, which fact shows that the capacity does not arise from a neutral gas layer on the electrodes acting as a condenser. It is probably due to a double layer of ions of the electrolyte and of the solvent at and on the electrodes, and hence to contact potential by these changes of concentration arising from electrolysis. The ratio between the inductance measurements at 600 and 1000 cycles is a constant which has the value 2·66, which shows that the inductance is nearly inversely proportional to the square of the frequency, the ratio for the square of the frequency used being 2·77. As this relation holds true for a leaky condenser, the cell seems to act as a resistance in series with a simple condenser with a leak. As the frequency is increased, the change in resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, are decreased, and both approach zero at infinite frequency. It is found that the ratio of the difference in the inductance in millihenries to the difference in the resistance in ohms between 600 and 1000 cycles is constant and equal to 2·00. The electrical capacities of the cells acting as leaky condensers have been measured by different consistent bridge methods. The capacities vary with the solution, size of electrodes, character of surface, and resistance, and range from 10 to 1000 microfarads for bright electrodes, and from 500 to 5000 microfarads for platinised electrodes. J. F. S.

Measurement of Electrolytic Conductivity. I. Theory of the Design of Conductivity Cells. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1916, **38**, 2431—2460).—A general discussion on the factors involved in the measurement of electrical conductivity. It is pointed out that theory demands the following alterations in the original Kohlrausch method of conductivity measurement: (1) the substitution of a high-frequency generator giving a pure sine wave of a single frequency, in place of the induction coil; (2) the use of a telephone tuned to the frequency employed; (3) the use of resistance units free from inductance and capacity; and (4) a proper and efficient use of the principle of electromagnetic shielding. The author then discusses the arrangement of the Wheatstone bridge and the distribution of the current in the bridge network with the object of ascertaining the most suitable conditions. A general theory of cell design is next con-

sidered, from which it is deduced that the area of the cross-section between the electrodes of a conductivity cell must not be less than a certain minimum value, which is completely fixed and determined by the audibility current of the telephone, the time required to make the bridge setting, the lowest specific conductivity which it is desired to include within the range of the cell, and the percentage accuracy demanded in the experiments. This practically means that the conductivity cell should be designed to fit the telephone. Three types of conductivity cells are described for use in measuring: (*a*) water or very dilute solutions; (*b*) dilute solutions; and (*c*) concentrated solutions. In connexion with the various cells, the author discusses: (1) the temperature-coefficient of the cell constant; (2) the choice of materials for the construction of cells; and (3) the elimination of polarisation. J. F. S.

Preparation of Conductivity Water. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 2460—2466).—A review of previous work on the preparation of conductivity water. It is shown that by distilling tap-water in Jena glass vessels and a tin condenser in contact with air, water of specific conductivity $0{\cdot}9 \times 10^{-6}$ at 25° can be obtained in one distillation. This specific conductivity is the same as that given by a saturated solution of carbonic acid under atmospheric conditions. A permanent lower value for water in contact with air is not possible, since slow absorption of carbon dioxide must take place until equilibrium is established unless air-tight vessels are employed. It is therefore unnecessary in conductivity work to invite the troubles involved in the preparation of purer water than the saturated carbonic acid solution. The aim should rather be to exclude all other conducting impurities except carbonic acid, and make an exact correction for this.

J. F. S.

Galvanic Ennobling of Metals. CH. M. VAN DEVENTER (*Zeitsch. physikal. Chem.*, 1916, **91**, 687—700. Compare A., 1908, ii, 12, 558; 1909, ii, 958; 1910, ii, 179).—The author has examined the ennobling of metals by alcohol–water layers with more exact apparatus than was possible previously. The *E.M.F.* set up in the following types of cells has been measured: $M^{I}|N/15\text{-}H_2SO_4|$ alcohol water$|M^{II}$ and $M^{I}|N/15\text{-}H_2SO_4|$water$|M^{II}$. The pairs of metals examined were Zn^{I}, Zn^{II}; Cd^{I}, Cd^{II}; Zn^{I}, Mg^{II}; Cd^{I}, Mg^{II}; Cd^{I}, Zn^{II}; and Sn^{I}, Cd^{II}. In each case in the first type of cell M^{I} constituted the positive pole, whereas in the second type it constitutes the negative pole. The values found were for the first type, Zn^{I}, Zn^{II} 280 millivolts, Cd^{I}, Cd^{II} 68 millivolts, Zn^{I}, Mg^{II} 425 millivolts, Cd^{I}, Mg^{II} 87 millivolts, Cd^{I}, Zn^{II} 68 millivolts, and Sn^{I}, Cd^{II} 185 millivolts. From the measurements of the cells of the second type, it is calculated that the metals M^{II} have been ennobled by the following amounts in the different cases: Zn^{I}, Zn^{II} *ca.* 200 millivolts, Cd^{I}, Cd^{II} 160 millivolts, Zn^{I}, Mg^{II} 1250 millivolts, Cd^{I}, Mg^{II} 1200 millivolts, Cd^{I} Z^{II} 250 millivolts, and Sn^{I}, Cd^{II} 350 millivolts. It is shown that the ennobled metal

becomes coated with a film of metal sulphate which does not dissolve in the alcohol–water mixture, and is a bad conductor of electricity. This ennobled metal is therefore to be regarded as an electrode of the second kind, and consequently the author's theory, previously published, as to the cause of the ennobling is no longer tenable. J. F. S.

Overvoltage Tables. III. Overvoltage and the Periodic Law. EDGAR NEWBERY (T., 1916, **109**, 1107—1117. Compare A., 1916, ii, 598).—Further measurements of cathodic overvoltage in $1N$-sulphuric acid and $1N$-sodium hydroxide solutions have been made, and the results show that the value for any particular electrode is closely connected with the position of the metal in the periodic table. Some difficulty is presented in choosing the normal value of the overvoltage, and this difficulty necessitates the investigation of the behaviour of the metal under as many different conditions as possible. In general, cathodic overvoltages in acid solution are more trustworthy than those in alkali solution, for there is only one cation present in the former, whilst the latter contains two.

The cathodic overvoltages fall into nine groups, the last eight of which correspond with groups 1—8 of the periodic table. The first group in the overvoltage table contains elements which show zero overvoltage under certain conditions. These elements are to be found also in one or more of the other groups. When overvoltages corresponding with more than one group are exhibited, the metal in question is known, in nearly all cases, to form compounds in which its valency corresponds with that of the metals of the groups in which it is placed.

Reviewing the overvoltage table as a whole, it is found that an increase of the overvoltage in two equal steps occurs in passing from group 0 to II, and this is followed by a gradual fall in the overvoltage in passing from the second to the eighth group.

Anodic overvoltages do not show the same degree of regularity, and this is probably connected with the fact that the solutions contain more than one anion, whilst a further disturbing factor is the formation of badly conducting oxides or peroxides.

H. M. D.

Effect of Pressure on the Potential of the Hydrogen Electrode. N. EDWARD LOOMIS and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2391—2396).—A number of experiments have been made to ascertain the effect of pressure on the potential of the hydrogen electrode. For this purpose, the *E.M.F.* of the cell $H_2|Pt,0{\cdot}1N\text{-}HCl|0{\cdot}1KCl,Hg_2Cl_2|Hg$ has been measured for pressures of hydrogen varying between 770·5 mm. and 709·5 mm. It is shown that the potential of the hydrogen electrode, at pressures near the atmospheric pressure, can be represented by the expression $E=RT/2F\,.\log_e H_2/H_2'$, in which H_2 and H_2' are the partial pressures. The average change in potential found is 0·00001751 volt per mm., which is only 0·3% larger than the value

0·00001746 volt calculated by the above formula. The mean value of the above cell at 25° is $0·42723 \pm 0·00003$ volt. J. F. S.

Tables for the Electromotive Estimation of Ion Concentration. J. MATULA (*Koll. Chem. Beihefte*, 1916, **8**, 299—336).—When the hydrogen electrode is combined with the normal calomel electrode, the *E.M.F.* of the cell at 20° and 760 mm. varies from 0·2835 to 0·6921 volt when the concentration of hydrogen ion falls from $1N$ to that of a neutral solution. The first table gives the calculated values of $[\dot{H}]$ for all *E.M.F.*'s within this range, the interval being 0·0001 volt. The second table gives the values of $[OH']$ for *E.M.F.*'s between 0·6921 and 1·1007 volt, which corresponds with the change from a neutral solution to a solution for which $[OH']=1N$.

When the pressure and temperature differ from the above values, corrections are supplied by supplementary tables. H. M. D.

Potential of the Mercury Electrode against the Mercurous Ion. G. A. LINHART (*J. Amer. Chem. Soc.*, 1916, **38**, 2356—2361).—The work of Ogg (A., 1899, ii, 14) on the potential of the mercurous ion, using solutions of mercurous nitrate, shows that the mercurous ion is $Hg_2^{\cdot\cdot}$, and that this is ionised further to $Hg^{\cdot}$ ions. The present paper deals with the nature of the mercurous ion, but instead of mercurous nitrate, mercurous perchlorate is used. The advantage of using this salt is that it is hydrolysed to a very slight extent, and the products of hydrolysis are soluble in water (Ley, A., 1904, ii, 465). Potential measurements have been made of cells of the type $Hg|Hg_2(ClO_4)_2HClO_4|$hydrogen electrode, in which the concentrations of perchloric acid varied from $0·0059N$ to $0·0817N$, and the mercurous perchlorate from $0·0000531N$ to $0·002750N$. From a large number of measurements it is shown that the best value for the potential of the mercurous electrode is $-0·7928$ volt. No regular deviations from the theoretical value of the *E.M.F.* are observed, from which it is deduced that no appreciable ionisation of the type $Hg_2^{\cdot\cdot} \rightleftarrows 2Hg^{\cdot}$ occurs even in the most dilute solution examined. J. F. S.

Tenth Normal Hydrochloric Acid Calomel Electrode. N. EDWARD LOOMIS and MERLE R. MEACHAM (*J. Amer. Chem. Soc.*, 1916, **38**, 2310—2316).—A long and careful series of *E.M.F.* measurements have been made of cells of the type $H_2,Pt|0·1NHCl|Hg_2Cl_2|Hg$ at 25° with the object of comparing this cell with the cell $H_2,Pt|0·1NHCl||0·1NKCl|Hg_2Cl_2|Hg$. It is found that the *E.M.F.* has the value $0·3988 \pm 0·0002$ volt at 25°, and that the hydrochloric acid calomel electrode is not as trustworthy as the potassium chloride calomel electrode. The constancy of the hydrochloric acid calomel electrode is greater, the greater the concentration of the acid, and below $0·03N$ the value cannot be depended on. The variations in the *E.M.F.* of this system are probably due to a chemical change in the calomel electrode, by which the potential varies with time. This series of experiments indicates that,

within the limits of experimental error, $N/10$-hydrochloric acid and $N/10$-potassium chloride are ionised to the same extent within limits of 1%. J. F. S.

Thermodynamic Properties of Silver and Lead Iodides. HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1916, **38**, 2295—2310). —A series of *E.M.F.* measurements of cells of the type $Pb|PbI_2|N/x KI|AgI|Ag$ have been made at 0° and 25°. The value of $x=10$ and 20. The object of the measurements was to ascertain whether the assumptions made in the Nernst heat theorem were justifiable, and to ascertain whether the results of Fischer (A., 1912, ii, 536, 1054), Braune and Koref (A., 1914, ii, 536), and Jones and Hartmann (A., 1915, ii, 308) were trustworthy, since these led to diametrically opposite conclusions with regard to the Nernst theorem. The following results were obtained: $N/x=0{\cdot}05$; at 25°, $\epsilon=0{\cdot}21157$ volt; at 0°, $\epsilon=0{\cdot}21475$ volt, whence the temperature-coefficient $=-0{\cdot}000127$ volt per degree and $U=11500$ cals. $N/x=0{\cdot}10$; at 25°, $\epsilon=0{\cdot}21069$ volt; at 0°, $\epsilon=0{\cdot}21415$ volt, whence the temperature-coefficient $=-0{\cdot}000138$ volt per degree and $U=11610$ calories. This gives as the mean heat of reaction of the change $Pb+2AgI=PbI_2+2Ag$, $U=11550\pm50$ cal.

This value agrees well with the value obtained from the best calorimetric data. The above value, when used to test the validity of the assumptions made in the Nernst heat theorem, leads to the conclusion that so far as the present experimental data with regard to specific heats may be employed the assumptions made in the theorem are justified. J. F. S.

Inclusions in the Silver Voltameter. T. W. RICHARDS and F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1916, **38**, 2044—2046). —A note emphasising the importance of the work of Vinal and Bovard (compare A., 1916, ii, 213) on the inclusion of mother liquors in the crystals deposited in the silver coulometer. The fact that platinum-black has a marked effect on the silver deposited, as shown by Vinal and Bovard, renders necessary the repetition of work by the authors on "volume effect" (compare A., 1915, ii, 81, 308) to see how far this source of error may have invalidated their results. W. G.

The Theory of Electrolytic Ions. VIII. The Mobility of some Inorganic Complex Ions. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **96**, 81—98. Compare A., 1916, ii, 312).—The transport numbers of sixteen cobalt and platinum complex salts have been determined by Hopfgartner's method, using cadmium anodes. The conductivity of the same salts has been determined, and a comparison of the two values leads to constitutions in accordance with Werner's views. The figures are tabulated. C. H. D.

The Ratio of the Boiling Point to the Critical Temperature. W. HERZ (*Zeitsch. anorg. Chem.*, 1916, **96**, 289—290. Compare *ibid.*, 1916, **95**, 253).—It has been shown by Guye (*Bull. Soc. chim.*,

1890, [iii], **4**, 262) that the boiling point of organic liquids under 10—20 mm. pressure is one-half of the critical temperature. It may be assumed that the boiling point under any given pressure is a constant fraction of the critical temperature. C. H. D.

Free Energy of Bromine Compounds. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 2348—2356).—A theoretical paper, in which the authors have calculated the free energy of the various forms of bromine, of the bromide and polybromide ions, and of all the known compounds of bromine with hydrogen and oxygen. In the calculations the available data have been reviewed, and the most probable values used in each case. The following values are obtained at 25° on the assumption that liquid bromine at this temperature possesses zero free energy; gaseous bromine, 755 cal.; solid bromine, 157 cal.; bromine in carbon tetrachloride solution of *N* strength, 389 cal.; aqueous bromine, 977 cal.; dissociated bromine atoms, 22328 cal.; gaseous hydrogen bromide, −12592 cal.; bromide ions (Br'), −24594 cal.; tribromide ions (Br_3'), −25267 cal.; pentabromide ions (Br_5'), −24400 cal.; aqueous hypobromous acid, −19739 cal.; and bromate ions (BrO_3'), 1690 cal. J. F. S.

Transition of Na_2SO_4. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1916, **91**, 676—686. Compare A., 1916, ii, 551).—A repetition of work previously published (*loc. cit.*). It is shown that no transition occurs at 385° with anhydrous sodium sulphate. The present experiments were made with a lever pressure apparatus, whereas the former pressure apparatus was hydrostatic in its action. The irregularities in the pressure–temperature curve previously obtained are shown to be due to loss of oil from the pressure cylinder. J. F. S.

The Determination of Dissociation Temperatures with the Aid of Cooling and Heating Curves, especially for Cobalto-cobaltic Oxide. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **96**, 64—70).—The dissociation temperature under atmospheric pressure is determined by heating the oxide in a porcelain tube in a carbon tube furnace. The cooling and heating curves are taken by means of a thermo-couple. Cobaltous oxide gives a smooth cooling curve in nitrogen or carbon dioxide, but in oxygen there is a change of direction at about 700°. On heating, dissociation sets in at 900°, whatever atmosphere be used. This temperature is higher the more compact the oxide. The most compact form, prepared from nitrate, has a dissociation temperature of 959°, Foote and Smith (A., 1908, ii, 847) having found 965° by the statical method. C. H. D.

The Atomic Theory. VIII. Space Filling and Mobility of Complex Inorganic Ions. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **96**, 217—230. Compare A., 1916, ii, 312).—The hypothesis proposed by Lorenz and his collaborators is tested by application to the case of inorganic complex ions of

known constitution. For this purpose the density of a number of complex cobalt and platinum salts has been determined, using pure benzene in the pycnometer. For dehydration, the hydrated salts are heated in a vacuum over barium oxide. The density at the absolute zero is calculated by adding 3% to the value at the ordinary temperature, this method being sufficiently accurate, as only the cube root of the molecular volume enters into the calculation of the dimensions of the ions. The electrical conductivities are taken from the authors' previous papers. The volumes of the chlorine and bromine ions are taken from those determined by optical means by Heydweiller (A., 1913, ii, 645), and the mobilities of fifteen inorganic complex ions are then calculated and compared with the experimental values. With the exception of the aquo-salts, all the ions examined fall within two limits, one of which is that given by close tetrahedral packing and the other by van der Waals's equation. Thus these, like the organic ions, move with a velocity corresponding with the law of Stokes and Einstein. Stereochemical conditions are without influence, and no difference is observed between ions with the co-ordination numbers 4 and 6. In many cases, the true volume falls with increasing apparent volume.

C. H. D.

The Kammerlingh Onnes Equation of Condition and the Theory of the Capillary Layer. G. BAKKER (*Zeitsch. physikal. Chem.*, 1916, **91**, 641—675. Compare A., 1915, ii, 614, 818; 1916, ii, 553).—A theoretical paper, in which the author further develops his theory of the capillary layer. It is shown by calculation that the theoretical part of the isotherm of Kammerlingh Onnes has a wave form. If ρ_1 and ρ_2 are respectively the densities of liquid and vapour in equilibrium and $\mu(\rho_1)$ and $\mu(\rho_2)$ the values of the corresponding thermodynamic potentials, then it is known that $\mu(\rho_1)=\mu(\rho_2)$. The author's theory then states that if between the liquid and vapour phase there is an horizontal capillary layer, $\mu(\rho_1)=\mu(\rho_2)=\mu[(\rho_1+\rho_2)/2]$. This can be expressed as follows: The density of that point on the labile portion of the isotherm where the thermodynamic potential has the same value as the usual liquid and vapour phase is the mean of the densities of the liquid and vapour. This statement has been proved in the case of carbon dioxide, where it is shown that at 0° $\mu(\rho_1)=3{\cdot}2616$, $\mu(\rho_2)=3{\cdot}3787$, and $\mu[(\rho_1+\rho_2)/2]=3{\cdot}2516$; other values are given for 10°, 20°, and 30°, all of which, like the above figures, show the truth of the statement. Hence, where the equation of condition fulfils the relationship $\mu(\rho_1)=\mu(\rho_2)$ there also are the conditions of the author's theory fulfilled. The radius of the smallest particle of vapour of carbon dioxide at 20° is calculated, and the value $R_{\text{min.}}=2{\cdot}25$ millimicrons found; a similar value for the smallest drop of liquid at the same temperature is found to be $R_{\text{min.}}=2$ millimicrons. It has been previously shown (*loc. cit.*) that the thickness of the capillary layer of carbon dioxide at 20° is $\zeta=2{\cdot}5\ \mu\mu$. Hence it follows that these two quantities are of the same order.

The same quantities have been deduced for 0°, and practically identical values obtained. If ρ_1 and ρ_2 are the densities of the liquid and vapour phases respectively, and ρ that of the capillary layer, ζ and R respectively the thickness and radius of the capillary layer, then for every curved capillary layer the following relationships hold: $[\rho-(\rho_1+\rho_2)/2]/\rho_1-\rho_2=\mp 5\zeta/24R$ and $[p_T-(p_1+p_2)/2]/p_1-p_2=\mp(R/2\zeta+5\zeta/24R)$, where p_T is the pressure in the long direction of the capillary layer and p_1 and p_2 the pressures of the homogeneous phases. The negative sign applies to liquid drops, and the positive sign to vapour bubbles. In the case of a horizontal capillary layer, $R=\infty$ and $p_1=p_2$, and the equations become $[\rho-(\rho_1+\rho_2)/2]/(\rho_1-\rho_2)=0$ or $\rho=(\rho_1+\rho_2)/2$.

As a consequence of the author's theory, the pressure in the long direction of a capillary layer (horizontal or curved) has the same value as the pressure at that point in the labile part of the theoretical isotherm where the thermodynamic potential has the same value as in the homogenecus phases which the capillary layer separates. It is shown by calculations that the Kammerlingh Onnes equation of condition confirms this deduction. If in an isothermal diagram the pressure (in the long direction) and the specific volume of every curved capillary layer are plotted, then the curve drawn through these points represents the labile portion of the isotherm for the given temperature. J. F. S.

Osmotic Pressure of Colloids. VI. Osmotic Pressure of Gelatin. WILHELM BILTZ, GÜNTHER BUGGE, and LUDWIG MEHLER (*Zeitsch. physikal. Chem.*, 1916, **91**, 705—721. Compare A., 1910, ii, 22, 673; 1911, ii, 702; 1913, i, 593, 832).—The authors have determined the osmotic pressure of solutions of nine varieties of gelatin, at 20°, at concentrations varying from 0·042% to 0·265%. From the osmotic pressure values the molecular weight has been calculated, and found to vary from 5500 to 31,000 for the different varieties. It is shown that the mineral matter contained in the gelatin has no influence on the osmotic pressure. A series of gold numbers was determined for the various samples, and a series of viscosity measurements was made for 0·05%, 0·10%, and 0·20% solutions of each variety after the solution had been made up twelve hours, twenty-four hours, and seventy-two hours. It is shown that, just as in the case of dextrin, the larger the molecular weight the better the protective action, and the greater the molecular weight the greater the viscosity. The authors therefore put forward as a general rule the statement: That in highly dispersed colloids the viscosity increases with increasing size of the particles, and the gold number, where such can be determined, decreases with increasing size of the particles. In an addendum details are given of the osmotic pressure of protein from horse serum. It is shown that the molecular weight is about 53,500. J. F. S.

Solubilities of Liquids in Liquids. Partition of the Lower Alcohols between Water and Cotton-seed Oil. B. B. WROTH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2316—2325).—The solubilities of methyl, ethyl, propyl, *iso*butyl,

and *iso*amyl alcohols have been determined in cotton-seed oil by calculation from the partition-coefficient between water and cotton-seed oil. If S_a and S_b represent respectively the solubilities of the alcohol in water and oil, C_a and C_b the concentrations in the same two solvents at equilibrium, and k the partition-coefficient, then $S_a/S_b = k = C_a/C_b$. The values of C_a and C_b were determined experimentally, and k calculated, and then either S_a or S_b was experimentally determined. The analysis of the two layers after partition was effected by means of an interferometer. The following values of k were obtained at 25°: methyl alcohol, 103·6: ethyl alcohol, 28·3; propyl alcohol, 6·41; *iso*butyl alcohol, 1·70; and *iso*amyl alcohol, 0·47. Methyl alcohol dissolves to the extent of 4·84 grams in 100 c.c. of cotton-seed oil, ethyl alcohol 21·2 grams in 100 c.c. of oil, and propyl, *iso*butyl, and *iso*amyl alcohols are soluble in all proportions. On calculating the solubility of methyl and ethyl alcohols in water from the above data, the figures 505 and 600 grams per 100 c.c. are obtained respectively. The authors point out that these figures represent ideal solubilities which could be realised if water and alcohol were separated by a semipermeable membrane through which only the alcohol molecules could pass.

J. F. S.

Crystal Stereochemistry. F. RINNE (*Zeitsch. anorg. Chem.*, 1916, **96**, [iv], 317—352).—The representations of crystal structures which have been deduced by the *X*-ray method, such as those put forward by W. H. and W. L. Bragg for rock-salt, zinc blende, pyrites, and calcspar, are to be regarded as crystal stereochemical formulæ. The conception of the crystal structure as purely atomic is held to be false (compare Niggli, A., 1916, ii, 300). Structural groups of atoms are clearly discernible, for instance, in the structures of calcite and corundum, and physico-chemical considerations clearly point to the existence of combination of a rigid character between the mathematically-considered distinct particles. The number of molecules contained within the unit space-lattice, however, bears no relation to the molecular complexity of the substance in the crystal. A crystal may be built up of similar, similarly orientated atoms, as in diamond; in other cases the atoms may appear in symmetrically distributed groups; or, finally, the structure may be partitionable into atomic complexes of a molecular character. The atomistic conception of Groth and the molecular theory of Bravais can thus be reconciled.

The forces of affinity between the atoms in the crystal can be supposed to act along the straight lines joining neighbouring particles, either the whole or a fraction of a valency being directed along each line. Thus in zinc blende, a zinc atom is tetrahedrally disposed towards four sulphur atoms, and may distribute its two valencies equally in the four directions towards these atoms. The affinities of the bivalent sulphur atom are similarly split up between four zinc atoms. In sodium chloride the affinity of each sodium or chlorine atom may be supposed to be partitioned among six neighbours. A connexion is traceable between such considerations and

Werner's theory of principal and subsidiary valencies (compare Pfeiffer, A., 1916, ii, 228).

The Laue diagram is of use in determining the principal zones and zone axes of a crystal structure, and to some extent the symmetry, although it only distinguishes eleven of the thirty-two classes. It also shows the relation between the forms of a polymorphous substance, between isomorphous substances, or between morphotropically related substances, such as the monoclinic and triclinic felspars.

The crystalline state is characterised by a three-dimensional periodic and straight-line orientation of similar particles, together with the capability of an indefinite extension of the structure, according to the same periodicity, in any direction. Amorphous substances lack this combination of properties. Liquid crystals occupy an intermediate position. Here the intermolecular forces are not strong enough to build up a space-lattice structure, but at the same time are sufficient to bring about a regular orientation of the particles with respect to a molecular axis. E. H. R.

Constitution and Fundamental Properties of Solids and Liquids. I. Solids. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1916, **38**, 2221—2295).—A long, theoretical paper, in which the work of Bragg is considered from the point of view of chemistry and its relation to the theories of chemical constitution, due to Werner, Stark, J. J. Thomson, and Lewis, and discussed in considerable detail. From the discussion the conclusion is drawn that the substances which have been studied by means of their *X*-ray spectra are not representative of compounds in general, since only polar compounds were considered. Solid polar compounds are, as a rule, built up of atoms bound together by residual valencies, and in these cases the whole crystal must be regarded as a single molecule. Solid, non-polar compounds consist, in general, of "group molecules," in which the atoms are held together by primary valencies. These group molecules are bound together by secondary valencies to form a large "crystal molecule," which includes the whole solid mass.

There is at present no justification for dividing intermolecular or interatomic forces into physical and chemical forces. It is better to regard all such forces as strictly chemical. Evaporation, condensation, solution, crystallisation, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena, and it is the object of the present paper to show that these processes can be so treated. From a consideration of specific heat, compressibility, and coefficient of expansion it is deduced that collisions do not occur between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces. The "time of relaxation" of the atoms of solids is calculated approximately from the thermal conductivity, and is shown to be of the order 10^{-7}—10^{-14} second. Somewhat similar results are obtained from a calculation based on the rate of evaporation in a vacuum. Consequently, the time required by an

atom of a solid to reach thermal equilibrium with the surrounding atoms is very small in comparison with the time required to make a single oscillation about its equilibrium position. The oscillations are thus very strongly damped. Since solid substances are, in general, held together by residual valencies rather than by primary valencies, there are few limitations to the number of compounds which can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the valency rules. A discussion is entered into on this point in the case of intermetallic compounds, minerals, solid solutions, and glasses. From a consideration of compressibility it is deduced that the attractive forces between atoms usually reach a maximum intensity when the distance between adjacent atoms in solids is increased by about $0{\cdot}6 \times 10^{-8}$ cm., that is, by about 10—30% of the normal distance. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between the atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption. Because of the small time of relaxation and because an atom approaching the surface is attracted by many atoms and later is repelled by a few atoms, it follows that the surfaces of solids are almost entirely inelastic to collisions of molecules impinging on them. As a result, nearly every molecule or atom striking a solid surface condenses, no matter what the temperature may be. Whilst condensed, it is held to the surface by forces similar to those holding solids together (primary or secondary valencies). At high temperatures evaporation may take place immediately after condensation, but at lower temperatures the condensed atom or molecule may remain indefinitely. A general discussion of sublimation is entered into. It is shown that the rate of evaporation, m, of a substance in a high vacuum is related to the pressure of the saturated vapour, p, by the expression $m=(pM/2\pi RT)^{\frac{1}{2}}$. Red phosphorus is not in agreement with this relationship.

The mechanism of the dissociation of a solid, such as calcium carbonate, is discussed. It is shown that when, according to the phase rule, separate phases of constant composition are present, the reaction must take place at the boundaries of these phases. This kinetic interpretation of the phase rule indicates the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers an explanation for the fact that hydrated crystals frequently fail to effloresce until scratched, and for the fact that completely dehydrated substances often absorb moisture with difficulty.

Adsorption is a direct consequence of the time lag between the condensation and subsequent evaporation of molecules; the adsorbed substance may be held to the surface by either primary or residual valencies; in either case it is better to regard the pheno-

mena as entirely chemical in character. A large number of experimental results are given to prove that adsorption is very frequently the result of the strongest kind of chemical union (primary valency) between the atoms of the adsorbed substance and the atoms of the solid.

It is shown that the action of a typical catalyst poison depends on the formation of a very stable film, one atom thick, over the surface of the catalyst. The chemical activity of a solid surface depends on (1) the nature of, (2) the arrangement of, and (3) the spacing of the atoms forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it.

A quantitative development of this theory of heterogeneous reactions is given, and a law of surface action, analogous to, but different from, the law of mass action, is proposed. This theory is in accord with, and affords an explanation of, Reichinstein's "Constant Sum Hypothesis." An application of this theory is made in the cases of heterogeneous gas reactions and to enzyme action.

J. F. S.

Protective Colloids. Radix Althaeae as Protective Colloid. A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1916, **19**, 177—191. Compare A., 1916, ii, 556).—The preparation and general properties of the colloidal solutions obtained by extracting the roots of marsh mallow are described. It is difficult to obtain optically clear extracts by filtration, but the addition of ethyl acetate is found to be of great assistance in the achievement of this result, and this reagent at the same time increases very markedly the stability of the solutions.

The behaviour of the solutions on dialysis, the phenomena of ageing, the influence of concentration and of electrolytes on the stability are described in detail. In an electrical field, the colloidal particles move to the anode, and this phenomenon is independent of the previous history of the solution. H. M. D.

Relation between the Chemical Constitution of Organic Compounds and their Capacity to Coagulate Acid Gold Hydrosols. JOHN A. GANN (*Koll. Chem. Beihefte*, 1916, **8**, 251—298).—The coagulating capacity of a large number of substances has been examined by measuring the "gold number," the substances investigated including albumoses, peptones, polypeptides, dyes, alkaloids, amines, and various heterocyclic compounds.

The results obtained show that the coagulating capacity of these nitrogen compounds depends on the presence of basic nitrogen groups, but that, apart from this, it varies considerably with the constitution of the substance. The auxochromic hydroxyl group increases the activity, although its effect is less marked than that of the amino-group. Certain configurations, such as those peculiar to the azines, thioazines, oxazines, and acridine derivatives also increase the coagulating activity, whilst chromophoric groups have

the opposite effect, and this is the more pronounced the more strongly acid the chromophoric group is. The less active a substance is found to be, the greater is the effect which is produced by the introduction of a new group.

With certain exceptions, the gold number for a particular substance is almost independent of the concentration of the coagulant. It varies, however, to some extent with the degree of dispersity, the concentration, and the acidity or alkalinity of the gold solution.

The coagulation process is in most cases to be regarded as brought about by ions, although in the case of the albumins it may be due to the mutual interaction of oppositely charged colloidal particles. The behaviour of gelatin shows that it may act either as a protective colloid or as a coagulant, and the actual results which have been obtained with this substance are discussed in detail with special reference to its amphoteric character.

H. M. D.

The Phenomena of "Clot" Formation. IV. The Diphasic Erosive Action of Salts on the Cholate Gel. S. B. SCHRYVER and MARY HEWLETT (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 361—372. Compare A., 1916, i, 448).—The erosive action of salts on the cholate gel containing added salts was investigated. If the concentration of the salts in the eroding solution are plotted as abscissæ and the amount of erosion as ordinates, a curve of diphasic character is obtained. The amount of erosion increases with increasing concentration to a maximum, after which it diminishes to a minimum; with further increase in concentration, the erosion increases continuously. The portion of the curve between the two minimal points is designated the "zone of instability." The breadth of this zone, and the amount of erosion within it, are functions of the amount of salt added to the gel. The amount of erosion and the breadth of the "zone of instability" vary with different eroding salts. The order of the action of chlorides is as follows: $LiCl > NaCl$ (generally) $> MgCl_2 > KCl$. This is the order of their action in increasing the permeability of vegetable cells. The action of sodium salts of organic acids was also investigated, and in all cases the general form of the curves was the same (diphasic). The antagonistic action of calcium salts was also examined, and it was found that relatively more calcium was necessary to antagonise the erosive action in the "zone of instability" than in higher concentration. The various physicochemical factors involved are discussed by the authors, and also the bearing of the results on certain biological problems.

S. B. S.

Fibrin and its Relationship to Certain Questions in Biology and the Chemistry of Colloids. X. The Two Kinds of Fibrin Sols and their Relations to the Conceptions of Colloidal Solutions. E. HEKMA (*Biochem. Zeitsch.*, 1916, **77**, 249—256).—Attention is directed to the distinction between the two kinds of sols, one of which is formed from solid

fibrin particles in the very finest state of subdivision which exist without water of imbibition, whilst the other is formed from particles of semi-fluid form with water of imbibition, which is taken up by fibrin in the presence of alkalis and acids. S. B. S.

Fibrin in its Relationship to Certain Questions in Biology and the Chemistry of Colloids. XI. The Three Kinds of Fibrin Gels. E. HEKMA (*Biochem. Zeitsch.*, 1916, **77**, 256—267).—A discussion of the processes of gel formation.
S. B. S.

The Law of Reaction Velocity and of Equilibrium in Gases. The Additivity of $C_v - \frac{3}{2}R$. New Determinations of the Integration Constants and of the Molecular Diameter. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1916, **96**, 1—28. Compare A., 1914, ii, 457; 1916, ii, 304).—It is assumed that when two molecules collide in an ideal gas, either the collision lasts only for a very short time, when no result is produced, or else it lasts for a time comparable with that between the collisions, in which case a chemical reaction takes place. Starting from the usual assumptions of thermodynamics and of the theory of gases, together with the author's principle of the additivity of the internal atomic heats, it is possible to calculate the integration constants of gas reactions and to compare them with the experimental values. All reactions in gases may be regarded as of the first or second order, all reactions of apparently higher order being regarded as due to successive collisions of pairs of molecules.

These considerations are applied to all the gas reactions of which the velocities have been determined. The constant K is found to have an average value of 10^{12} mols. per c.c. per second, but the values for different reactions given vary between $2 \cdot 5 \times 10^{11}$ and 10^{16}. The heat of activation, q_0, is also found to be constant. For the case of nitrosyl chloride, the molecular diameter is calculated to be $3 \cdot 45 \times 10^{-8}$ cm. C. H. D.

The Velocity of Hydration of Metaphosphoric Acid. II. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1916, **96**, 99—107. Compare A., 1911, ii, 974).—The molecular weight of orthophosphoric acid in dilute glacial acetic acid solution corresponds with the simplest formula. The hydration of metaphosphoric acid is affected by the presence of either acetic or sulphuric acid in the solution, and the results suggest that the unimolecular acid has the greater velocity of hydration. The meta-acid is rapidly hydrated by dissolving in concentrated hydrochloric or nitric acid. The course of the reaction when phosphoric oxide is dissolved in water has been followed by titration with sodium hydroxide, using methyl-orange and phenolphthalein as indicators. Only the meta-acid is obtained in ice-cooled water. The results obtained in previous papers are summarised. C. H. D.

The Reaction of both the Ions and the Non-ionised Forms of Acids, Bases, and Salts: the Reaction of Methyl Iodide with Sodium, Potassium, and Lithium Ethoxides at 0°. BESSIE M. BROWN and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2145—2156. Compare Robertson, A., 1915, ii, 406, 681; Taylor and Acree, A., 1916, ii, 423).—A study of the rates of reaction between methyl iodide and sodium, potassium, and lithium ethoxides at 0°, the concentrations of the ethoxides varying between N/1 and N/32. The activity, K_i, of unit concentrations of the ethoxide ion, calculated from the data obtained, was the same whichever ethoxide was used, and the average value was 0·0051 at 0°. The value, K_m, for the non-ionised molecule varied with the ethoxide, being about 0·0030 for sodium ethoxide, 0·0034 for potassium ethoxide, and 0·0020 for lithium ethoxide. The solutions used being concentrated, the values obtained will need to be corrected later for the various physical constants, such as viscosity, specific gravity, etc., which are modified by the different substances present. The results obtained support the general theory as to the activity of both the ions and the non-ionised portion of acids, bases, and salts. W. G.

The Hydrolysis of Hexahydropyrimidine. GERALD E. K. BRANCH (*J. Amer. Chem. Soc.*, 1916, **38**, 2466—2474. Compare Titherley and Branch, T., 1913, **103**, 330).—In the first part of the paper the author discusses the effect of the hydrogen ion on additive reactions of an allelotropic mixture, which involves a tautomeric shift about a nitrogen atom, and points out that in such cases the hydrogen ion may be expected to act as a negative catalyst. The rate of hydrolysis of hexahydropyrimidine was measured at two different temperatures and with varying hydrogen-ion concentrations, the results obtained being in agreement with the theory. The reaction was found to have a high temperature-coefficient, the mean values of K_2 found being $3·67 . 10^{-3}$ at 25° and $1·46 . 10^{-3}$ at 18·4°. Alcohol increased the rate of hydrolysis of hexahydropyrimidine. At low concentrations, sodium chloride increased the rate of this reaction, but at higher concentrations it acted as a negative catalyst. W. G.

A Period of Induction in the Dehydration of some Crystalline Hydrates. WILLIAM NORMAN RAE (T., 1916, **109**, 1229—1236).—The rate of dehydration of crystals of copper sulphate pentahydrate has been investigated with the object of determining the cause of the induction period which is associated with the process. Mechanical stirring of the finely powdered crystals increases the initial rate of dehydration, and inoculation with crystals of the trihydrate produces the same effect. In the later stages, the progress of the dehydration is in approximate agreement with the equation for a unimolecular reaction.

The results obtained in respect of the initial period suggest a close analogy with the behaviour of supersaturated solutions, and if this view is correct, it may be that the induction period is to

be referred to the relatively high vapour pressure of very small particles of copper sulphate trihydrate as compared with the vapour pressure of larger particles. By taking into account the influence of the size of the particles on the vapour pressure of the lower hydrate, it is unnecessary to assume the intermediate formation of an unstable amorphous form, a view advanced by Partington (T., 1911, **99**, 466) to account for his observations on the variation in the vapour pressure of crystalline hydrates. H. M. D.

Saponification of some Esters of Pyrroledicarboxylic Acid at 50°. G. Korschun and A. Gounder (*Bull. Soc. chim.*, 1916, [iv], **19**, 366—392; *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 637—667). —A continuation of previous work (compare A., 1916, i, 606; ii, 525). Starting with ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, the authors have examined the effect of introducing a methyl group into position 1, and then substituting this in turn by an amino-, a carbamido-, and a phenyl group on the rate of saponification of the first and second carbethoxy-groups by potassium hydroxide at 50°. The saponification constant for each group is given in each case, but as the concentrations of alkali used vary, these cannot be tabulated. The introduction of the methyl group into position 1 increases the ease of saponification of the first carbethoxy-group of the di-ester. The introduction of the amino-group into position 1 renders it more difficult to saponify the monoethyl ester than in the case of either the trimethyl- or the dimethyl-pyrroledicarboxylic acid monoethyl ester. The results obtained when a carbamido-group is introduced into position, are difficult to interpret, and require further work to be done with the di-ester. The results obtained with a phenyl group in position 1 are unsatisfactory, owing to the instability of the monoethyl ester of 1-phenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid.

Determinations were also made in the cases of diethyl 2 : 5-diphenylpyrrole-3 : 4-dicarboxylate, diethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, and 3-carbethoxy-2 : 4-dimethylpyrrole-5-carboxylic acid. W. G.

Dissociation of Salicylic Acid. J. A. Christiansen (*Zeitsch. physikal. Chem.*, 1916, **91**, 701—704. Compare Bauer and Orthner, A., 1916, ii, 232).—The author has repeated the experiments of Bauer and Orthner on the dissociation of salicylic acid. It is shown that at 203° salicylic acid is completely dissociated, whereas it had previously been stated by Bauer and Orthner that the reaction only occurred to the extent of 25% at this temperature. The present author is of the opinion that the low result is due to the shortness of duration of the experiments. J. F. S.

Catalysis of Hydrogen and Oxygen Mixtures at the Ordinary Temperature by Moistened Contact Substances. K. A. Hofmann and Ralf Ebert (*Ber.*, 1916, **49**, 2369—2389).—A summary of some experiments on the union of hydrogen with oxygen in the presence of various contact catalysts is given. Most of the conclusions have been given before in many other papers

by one of the authors in recent years, and have been embodied in his method for estimating hydrogen (see A., 1916, ii, 636). The points of particular interest may be stated again.

The catalysis of the union of hydrogen with oxygen at metallic surfaces is an electromotive process, and the reaction is comparable with that in the gas chain of a Groves's cell. Oxygen takes a much longer time to acquire the necessary potential than hydrogen does at platinum, iridium, or palladium surfaces, and the combination of hydrogen with oxygen in a mixture can therefore be accelerated by a preliminary loading of the contact substance with oxygen. The oxidation-potential of oxygen is higher in an acid medium than in an alkaline or neutral one.

It is particularly emphasised that it is not sufficient to "activate" one reagent in order to accelerate a reaction. Each participant must be activated. For this purpose, combinations of catalysts must be used, the most powerful in the case of hydrogen and oxygen being palladium and small quantities of most finely divided palladium in the presence of sodium hydrogen carbonate. The addition of hydrogen or oxygen "carriers" is not advisable, as they will so reduce the potential of the oxygen or the hydrogen, as the case may be, that their influence may be more than nullified.

J. C. W.

The Dual Theory of Acid Catalysis. A Comparison of the Activities of certain Strong Acids. Harry Medforth Dawson and Thomas William Crann (T., 1916, **109**, 1262—1277. Compare T., 1913, **103**, 2135; 1915, **107**, 1426).—With a view to the further examination of the dual theory of acid catalysis, measurements have been made of the rate of isomeric change of acetone under the catalytic influence of hydrobromic, trichloroacetic, trichlorobutyric, and *p*-toluenesulphonic acids at different concentrations.

The velocity-coefficients of the ionised acid, k_H, and the non-ionised acid, k_M, are derived from the equations $k_H = V_1(1-\alpha_1) - V_2(1-\alpha_2)/\alpha_1 - \alpha_2$ and $k_M = V_2\alpha_1 - V_1\alpha_2/\alpha_1 - \alpha_2$, in which V_1 and V_2 are the equivalent velocities of the reaction, and α_1 and α_2 the corresponding degrees of ionisation of the acid. The α-values required were obtained from conductivity data.

The weighted mean values of k_H and k_M are employed to calculate the velocities of reaction, and the results are shown to be in satisfactory agreement with the measured velocities, thus affording further evidence in favour of the dual activity of the acids.

The ratio k_M/k_H is in all cases greater than unity, and this shows that the acid is more active in the non-ionised condition, a result previously obtained for hydrochloric acid. On the assumption that $\alpha = \Lambda/\Lambda_\infty$, the value of the ratio decreases in the order hydrochloric, hydrobromic, trichloroacetic, *p*-toluenesulphonic, and trichlorobutyric acids. For trichlorobutyric acid, k_M/k_H is nearly equal to unity, and it follows that the catalytic activity of this acid is determined solely by the concentration and is independent of the degree of ionisation.

When the k_M/k_H values are compared with those obtained by other observers in experiments on the hydrolysis of ethyl acetate and sucrose, very considerable differences are found in the case of trichloroacetic and trichlorobutyric acids. For the latter acid, the two values of k_M/k_H are approximately as 20:1, and it would therefore seem that the magnitude of the ratio varies according to the nature of the catalysed reaction.

Incidentally, it is shown that the dual hypothesis is in harmony with Arrhenius's equation, $v=k_Hc\alpha+k'_M(c\alpha)^2$, so long as weak acids are in question.

The fact that the catalytic activity of the strong acids, as measured by the equivalent velocity, V, may be represented by the equation $V=V_0+a\sqrt[3]{c}$, in which V_0 is the velocity for $c=0$ and a is a constant (Snethlage, A., 1915, ii, 615, 825), is shown to be a consequence of the dual hypothesis, and is to be attributed to the circumstance that the conductivity varies with the concentration of the acid in fairly close agreement with Kohlrausch's equation, $\Lambda=\Lambda_\infty-b\sqrt[3]{c}$. H. M. D.

The Atomic Weights. O. D. Chwolson (*Bull. Acad. Imp. Sci. Petrograd*, 1915, 1841—1852).—A theoretical paper in which the author considers how near the atomic weights of the elements approach to some multiple of four (atomic weight of helium). By arranging the numbers under differing groups, allowing for possible errors in the values used (Landolt's tables, 1912) the author arrives at the view that the atomic weights are considerably condensed around numbers of the type $4n$, and that the number of values coming between $4n$ and $4n-2$ considerably exceeds those coming between $4n$ and $4n+2$. W. G.

The Law of the Periodicity of the Elements, and the Natural Periodic System. S. Silbermann (*Ber.*, 1916, **49**, 2219—2222).—In connexion with the larger question of the "Creation, and the origin of energy and matter," the author has developed the idea that the inert gases are the parent substances of all the elements. He regards argon as a mixture of a gas with the atomic weight 36·4 and another with the weight 153. If the elements are grouped in the order of their atomic weights in periods from one amphoteric element to the next (H to Li, Gl to Mg, Al to Sc, Ti to Yt, Zr to Ce, Pr to Tm, Yb to U), each period will be found to contain an inert gas, including the unknown gas with atomic weight 153. The weights can be so plotted that the inert gases fall on a vertical line, when the other elements will fall on parallel straight lines which cross this. Immediately to the left of the line will be found the most electronegative elements, to the right the electropositive, and these characteristics will be found to become less and less pronounced the more remote the element is from the line. Connecting elements of one chemical family by other lines, it becomes apparent that the most perfect agreement among the elements of a particular family is when the connecting line approaches more nearly to a straight line parallel

to the inert gas line. A diagram which embodies these features is given. J. C. W.

Molecular Weight Determinations in Bromine by the Air-current Method. ROBERT WRIGHT (T., 1916, **109**, 1134—1139).—The vapour pressures of pure bromine and of bromine containing foreign substances dissolved in it are measured at the same temperature by the air-current method. The apparatus was designed so that the bromine vapour can only come into contact with glass and the absorbing solution. Molecular weights calculated from the Raoult equation gave for bromoform, antimony tribromide, stannic bromide, and iodine monobromide values corresponding with the empirical formulæ. The value for sulphur shows that it is present in the form of diatomic molecules.
H. M. D.

The "Cyclic Theory" of the Constitution of Complex Inorganic Compounds: A Criticism. EUSTACE EBENEZER TURNER (T., 1916, **109**, 1130—1134).—A criticism of Friend's views on valency (T., 1908, **93**, 260, 1006). H. M. D.

Double Bond and the Electron Theory. L. SPIEGEL (*Biochem. Zeitsch.*, 1916, **76**, 313).—A claim for priority.
S. B. S.

New Application of the Bunsen Valve. ALAN LEIGHTON (*J. Ind. Eng. Chem.*, 1916, **8**, 1037—1038).—A Bunsen valve may be inserted in the tube connecting a water-pump with a vessel from which the air is being exhausted; any back-flow of water from the pump to the vessel, due to accidental decrease in the water pressure, is thus prevented. Thick-walled caoutchouc tubing should be used in constructing the valve or the modification of the Bunsen valve described by Kreider (A., 1896, ii, 161) may be employed.
W. P. S.

An Electrically Heated Vacuum Desiccator. T. BRAILSFORD ROBERTSON and CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1916, **27**, 429—431).—The apparatus consists of a double-walled copper chamber maintained at the desired temperature by electrical heating elements, for a description of which the original paper must be consulted. H. W. B.

Simple Mercury Sealed Ether Still. O. C. SMITH and D. G. MORGAN (*J. Ind. Eng. Chem.*, 1916, **8**, 1039).—The distillation flask is closed by a cork, which is inserted so that its upper surface is a short distance below the top of the neck. This cork carries a short piece of glass tubing, over the top of which is fitted the end of the condenser. Mercury is now poured into the neck of the flask until the space above the cork is filled. A flask similarly fitted serves as the receiver, but the cork closing this flask carries a second tube, which is connected with a reflux apparatus to

prevent loss of ether vapour. The distillation flask is heated by an ordinary electric bulb fitted below a tripod supporting the flask, and is surrounded by a metal shield. W. P. S.

Inorganic Chemistry.

Apparatus for the Recovery of Bromine. C. H. COLLINGS (*Chem. News*, 1916, **114**, 259—260).—Waste liquors from estimations of urea by the hypobromite method are collected, and measured quantities are decomposed by hydrochloric acid in a suitable bottle; the liberated bromine is absorbed in a vessel containing sodium hydroxide solution, and sodium hypobromite is thus re-formed. A current of air, passed previously through sodium hydroxide solution, is drawn through the apparatus to carry over the bromine vapour, tapped funnels are provided for introducing more waste liquor and sodium hydroxide respectively, and the bottle and absorption apparatus are fitted with siphons for drawing off their contents when necessary. W. P. S.

Colloidal Iodine. H. BORDIER and G. ROY (*Compt. rend.*, 1916, **163**, 567—569. Compare A., 1916, i, 630, ii, 547).—Ultramicroscopic examination confirms the view (*loc. cit.*) that iodine in pure water is in a colloidal state, but in the form of granules too small to be seen even with an ultramicroscope. If, however, it is prepared in the form of a protected colloid in the presence of a suitable proportion of gelatin, these very minute granules unite to form particles large enough to be visible under an ultramicroscope. If this pseudo-solution is submitted in a U-tube to a potential difference of 62 volts, it is sharply concentrated at the side of the positive electrode, the discharge of the particles is complete, and the iodine is obtained in crystalline form. In the presence of a small quantity of sodium thiosulphate the discharge is not complete, and there is simply coagulation. W. G.

The Electrolytic Preparation of Hydroxylamine Hydrochloride. E. P. SCHOCH and R. H. PRITCHETT (*J. Amer. Chem. Soc.*, 1916, **38**, 2042—2044).—The method is designed for preparing hydroxylamine hydrochloride on a large scale. The apparatus used is identical with that of Tafel (compare A., 1902, ii, 559), except that the anode used is a lead pipe or rod about 1 inch in diameter instead of the graphite rod used by him. The cathode compartment is filled with a mixture of three volumes of water to one volume of hydrochloric acid (D 1·20). The anode liquid is cooled by causing it to circulate continually through a lead pipe coil immersed in the freezing mixture used to cool the cathode liquid. The current used is 50 amperes at 25 volts, and the

nitric acid (D 1·4) mixed with one volume of water is run into the cathode compartment at the rate of 30 c.c. per hour, the addition being allowed to proceed for two and a-half hours. The cathode liquid is concentrated in a vacuum on a water-bath, and the hydroxylamine hydrochloride freed from ammonium chloride by crystallisation from alcohol. W. G.

The "Supposed" Importance of Nitrous Acid in the Formation of Hydrazoic Acid by the Oxidation of Hydrazine. FRITZ SOMMER (*Zeitsch. anorg. Chem.*, 1916, **96**, 75—80. Compare A., 1914, ii, 266).—A reply to Browne and Overman (A., 1916, ii, 245). The author maintains his view as to the mechanism of the oxidation of hydrazine with the intermediate formation of nitrous acid. C. H. D.

The System Phosphorus in Light of the Theory of Allotropy. A. SMITS and S. C. BOKHORST (*Zeitsch. physikal. Chem.*, 1916, **91**, 756—757. Compare A., 1916, ii, 317).—An addendum to the previous paper. It is shown that the sublimation temperature of violet phosphorus is 690·9°. J. F. S.

The Basicity of Hypophosphoric Acid. ILSE MÜLLER (*Zeitsch. anorg. Chem.*, 1916, **96**, 29—63).—In order to determine whether hypophosphoric acid has the single or double formula, the hydrogen-ion concentration in solutions of the salts $Na_2PO_3,5H_2O$ and $NaHPO_3,3H_2O$ has been determined, alizarin-yellow, methyl-red, and *p*-nitrophenol being used as indicators. The salts may be estimated by oxidation with nitric acid, followed by ignition, $NaHPO_3$ being converted into $NaPO_3$ and Na_2PO_3 into $Na_4P_2O_7$. In this way the equilibrium in the system $Na_2O-P_2O_4-H_2O$ has been examined, the following four salts being found to exist at 30°: $Na_2PO_3,5H_2O$, $Na_3H(PO_3)_2,9H_2O$, $NaHPO_3,3H_2O$, and $NaH_3(PO_3)_2,2H_2O$, whilst the two salts $Na_3H_5(PO_3)_4$ and $Na_5H_3(PO_3)_4,20H_2O$ may also have a limited range of existence. These formulæ do not prove that the acid has the double formula $H_4P_2O_6$, as they may possibly be associated compounds of the salts with the acid and with one another. The solubility curves of the first three salts mentioned above have been determined exactly.

Guanidinium hypophosphate (Rosenheim and Pinsker, A., 1910, ii, 708) has the composition $(CH_6N_3)_2PO_3,H_2O$. Sodium molybdo-hypophosphate (Parravano and Marini, A., 1906, ii, 744) has the composition $Na_2[P(Mo_2O_7)_3],8H_2O$. Hexa-amminocobaltic salts yield a characteristic salt, $[Co(NH_3)_6]NaP_2O_6,3H_2O$, which crystallises from hot concentrated solutions in brown, glistening scales. There is no complete analogy between hypophosphoric and pyrophosphoric acids. C. H. D.

Simultaneous Separation of Two Forms of Silicic Acid from the same Silicate. GUSTAV TSCHERMAK (*Chem. Zentr.*, 1916, ii, 302; from *Sitzungsber. K. Akad. Wiss. Vienna*, 1916, **125**).—Dilute mineral acids decompose forster-

ite, Mg_2SiO_4, yielding the sol of orthosilicic acid, whereas the most concentrated acids give a precipitate of metasilicic acid; with mineral acids of medium concentration, the two silicic acids are formed simultaneously. Similar silicates which have so far been investigated (Fe_2SiO_4, $MgCaSiO_4$, Zn_2SiO_4) yielded only the ortho-acid. The atomic volume of forsterite is less than that of the remaining silicates; hence, in addition to the chemical energy, a volume energy is available for the formation of orthosilicic acid from forsterite, which is much greater than that available for the formation of the meta-acid from the same silicate. Lievrite, $FeHFe_2CaSi_2O_9$, resembles forsterite in its behaviour towards acids, and yields both forms of silicic acid when treated with mineral acid of medium concentration. The atomic volume of lievrite is identical with that of forsterite, and, further, a corresponding atomic net can be constructed in which the space relationships of the observed crystal dimensions are analogous. In doubtful cases the behaviour towards dilute acid leads to the recognition of that silicic acid from which the silicate is theoretically derived. H. W.

Concentration of Radium in Carnotite Ores. ALBERT G. LOOMIS and HERMAN SCHLUNDT (*J. Ind. Eng. Chem.*, 1916, **8**, 990—996).—A low-grade American carnotite ore was digested with sulphuric acid at 250—300° for thirty minutes, the mass then treated with a large volume of water, and the insoluble portion subjected to differential sedimentation. Practically all the vanadium and uranium compounds present were dissolved, whilst the fine sands contained 87% of the radium, the concentration of the latter in the sands being from twenty to twenty-eight times more than it was in the ore. A similar separation and concentration of the radium was effected by fusing the ore with sodium hydrogen sulphate or with salt-cake; digestion with sulphurous acid at the ordinary temperature and differential sedimentation of the products yielded a sand containing 85% of the radium at a concentration of ten to twelve times that of the ore. By digesting these concentrates with sulphuric acid, or by fusing them with a mixture of potassium and sodium carbonates, a residue of crude sulphates was obtained containing 80% of the radium at a concentration varying from 150 to 300 times that of the ore. A few experiments were made to ascertain whether treatment of carnotite with chlorine water or carbon dioxide effected a selective extraction of the radium, but the results obtained were not very promising. The radium content of the tailings obtained by treating the ore with sulphuric acid or sodium hydrogen sulphate was estimated by the emanation method and found to exceed the values obtained by comparison of the radiation from equal areas of ore and tailings; it is suggested that, in the latter method, comparisons should be made against standardised tailings instead of ore. W. P. S.

Ammonium Silicate. ROBERT SCHWARZ (*Ber.*, 1916, **49**, 2358—2364).—Evidence of the existence of ammonium silicate is given. The solubility of silicic acid in ammonia solutions depends

on the concentration of ammonia, the temperature, and the water content and physical form of the acid. The solubility of the hydrate, $3SiO_2,H_2O$, in $3N$-ammonia at 18° reaches a maximum in about two hundred hours, corresponding with about one-fiftieth of the amount of acid required to form a metasilicate; in $10N$-ammonia at 100° the solubility after one hour reaches 84·3%; in $2N$-ammonia at 100° the hydrate dissolves to the extent of 55·7%, ignited precipitated silica to the extent of 24·4%, both in one hour, whilst finely powdered quartz only loses 2·7% of its weight in a day. Solutions obtained in the hot way have the appearance of colloidal solutions, but the cold preparations are clear. Inasmuch as the conductivity of the ammonia solution rises with time (in the case of the hydrate, with negative acceleration: in the case of the anhydride, with positive acceleration during the first one hundred hours), the formation of a true ammonium silicate seems to be certain.

Although the salt cannot well be isolated, the nearly related *tetraethylammonium silicate*, $(NEt_4)_2SiO_3$, can be obtained as a hygroscopic, amorphous powder by heating the silicic acid hydrate with 10% tetraethylammonium hydroxide in a sealed tube at 80°.

J. C. W.

The Chromates of Silver and the Solid Solutions with Nitrates. FRITZ KÖHLER (*Zeitsch. anorg. Chem.*, 1916, **96**, 207—216).—The properties of silver chromate differ widely with the method of preparation, and contradictory descriptions are therefore found in the literature. In the rhythmical precipitation of silver chromate by means of ammonium dichromate (A., 1916, ii, 554) the small crystals of ammonium nitrate which also separate rhythmically are coloured by silver chromate, being yellowish-green to red, according to the concentration. Similar coloured crystals are obtained when a solution of ammonium nitrate containing a little ammonium dichromate is mixed with a drop of silver nitrate and allowed to evaporate on a glass slide. Exactly similar crystals are obtained when potassium dichromate is used.

Both silver chromate and dichromate can take small quantities of ammonium or potassium nitrate into solid solution. The colour of pure silver chromate is always greenish-black, and the red substance, supposed to be a separate modification, is a mixture of silver chromate and the solid solutions with nitrates. C. H. D.

Vanadates of Glucinum. PAUL H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1916, **38**, 2361—2366).—The author shows that the products obtained by the addition of solutions of soluble vanadates to solutions of glucinum salts are mixtures of variable composition, and not definite salts. The compound glucinum metavanadate, $Be(VO_3)_2,4H_2O$, has been obtained by boiling equimolecular quantities of glucinum hydroxide and vanadium pentoxide with water for about an hour; the solution was filtered and concentrated to about 40 c.c., which usually yielded an orange-red syrup. This, while hot, was poured into a large volume of 95% alcohol, when a

copious deposit of yellow particles was produced, which in twenty-four hours had settled to a thick layer of yellow crystals. Viewed under the microscope, these were seen to be yellow, waxy plates. The crystals are isometric, being cubes modified by the octahedron. Glucinum metavanadate is sparingly soluble in cold water, 1 per 1000, but readily so in hot water, and has a strong tendency to supersaturate. It is practically insoluble in chloroform, ether, or absolute alcohol, but is soluble in pyridine to about the same extent as in water. The crystals have D 2·273, and lose the whole of their water of crystallisation over sulphuric acid. J. F. S.

The Atomic Weight of Lead. W. Œchsner de Coninck and Gerard (*Compt. rend.*, 1916, **163**, 514—515).—The lead used was carefully purified by treatment with acids, and from it a sample of pure anhydrous lead nitrate was prepared. A weighed quantity of this was ignited, and the lead oxide left was weighed. The mean value for the atomic weight of lead obtained from four such determinations was 206·98. Using lead obtained from uranium minerals, eliminating as far as possible all lead not of radioactive origin, the value obtained was 206·71. W. G.

Arsenates of Lead. II. Equilibrium in the System, $PbO-As_2O_5-H_2O$. C. C. McDonnell and C. M. Smith (*J. Amer. Chem. Soc.*, 1916, **38**, 2366—2369. Compare A., 1916, ii, 620). The system $PbO-As_2O_5-H_2O$ has been examined by shaking quantities of 2 grams of lead hydrogen orthoarsenate, $PbHAsO_4$, with quantities of 0·0338*N*-ammonia solution (90—180 c.c.) for fourteen hours at 32°. The solutions were filtered and the filtrate analysed. From the results, it is shown that lead orthoarsenate is first produced, the supernatant liquid remaining constant in composition until the conversion is complete, and during this period having the composition $(NH_4)_2HAsO_4$. After the change is complete, solid solutions, varying from lead orthoarsenate to a basic arsenate, are produced, beyond which no change occurs. Lead orthoarsenate was prepared by treating lead hydrogen orthoarsenate with the theoretical amount of *N*/10-ammonia. It is an amorphous powder, D^{15} 7·00. J. F. S.

The Action of Ammonium Monosulphide on Mercuric Sulphide. A. Christensen (*Ber. Deut. pharm. Ges.*, 1916, **26**, 261—266).—Aqueous solutions of ammonium monosulphide when poured on mercuric oxalate, acetate, sulphate, chloride, iodide, or other mercuric salt become yellow in colour, due to the partial liberation of sulphur, with formation of ammonium polysulphide. In confirmation of this explanation, the author adduces the results of an analytical examination of the solution and of the residual solid; the latter is found to consist of a mixture of mercuric sulphide with free mercury. Yellow mercuric oxide, in particular, imparts a yellow colour to ammonium sulphide solution, but the solution gradually loses its colour, because the sulphur slowly returns to the solid matter, with formation of vermilion. Mercuric cyanide

when treated with ammonium sulphide solution is comparatively rapidly converted into vermilion, but the solution throughout remains colourless. Mercuric sulphide, already formed, does not yield sulphur to ammonium sulphide solution, so that the liberation of sulphur must occur during the interaction of the mercuric salt and the ammonium sulphide.

Sodium sulphide resembles ammonium sulphide in giving, with mercuric salts, precipitates containing free mercury, although in this case the abnormality is less marked. D. F. T.

Purification and Atomic Weight of Yttrium. B. SMITH HOPKINS and CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1916, **38**, 2332—2347).—An historical résumé of the atomic weight determinations of yttrium from 1873 is given. The authors continue the work previously published (A., 1913, ii, 508) on the purification of yttrium salts. They examine in the present paper the chromate method, the ammonia method, and the nitrite method of purification. It is shown that fractional precipitation with potassium chromate is capable of removing considerable quantities of the other rare earths from yttrium, but it will not remove all the erbium or holmium; fractional precipitation with dilute ammonia is tedious and does not produce pure yttria, and fractionation with sodium nitrite is both rapid and effective in freeing yttrium from holmium and erbium. In examining the methods used for the determination of the atomic weight, the authors find that the sulphate synthesis method is not trustworthy, since the value may be made to vary widely by changing the length of time and temperature of ignition. The hydrates $Y_2(SO_4)_3,8H_2O$ and $YCl_3,6H_2O$ are found to be too variable to permit of their use in atomic weight work. The atomic weight of yttrium was determined from the ratio $Y_2O_3:2YCl_3$, using material obtained by means of the above methods of purification, six different fractions being employed. The method was identical with that previously described (*loc. cit.*). As a mean of six determinations, the value $Y = 88{\cdot}9$ was obtained, the individual experiments varying between 88·80 and 89·06. J. F. S.

Electrolysis and Purification of Gallium. HORACE S. UHLER and PHILIP E. BROWNING (*Amer. J. Sci.*, 1916, [iv], **42**, 389—398).—An alkaline solution of gallium hydroxide in sodium hydroxide, on electrolysis at the ordinary temperature, usually deposits gallium as liquid globules on the cathode. The authors find that such a solution obtained after the separation of indium (A., 1916, ii, 330) on electrolysis at 0° by a current of 0·28 amp., $D_A = 0{\cdot}007$ amp. per sq. cm. and $D_C = 6$ amp. per sq. cm., deposits the metal in black, arborescent forms. The deposition of the "gallium tree" depends on the alkalinity of the solution and the curvature of the surface of the liquid globule. A number of photographs of the trees are reproduced in the paper. The trees are hard, like the solid gallium produced in any other manner, and are permanent so long as they are kept at a temperature 10° below the melting

point. They are black in colour, although this is chiefly superficial, and when cut present the usual silvery lustre of pure gallium. When placed in water, gas is slowly evolved, and the metal becomes coated with black, grey, and white patches. A separation of gallium and indium may be effected (i) by solution of gallium hydroxide from the mixed hydroxides by sodium hydroxide; (ii) by crystallisation of the ammonium alums from 70% alcohol; and (iii) by crystallisation of the cæsium alums. In the last case it is shown that a gallium preparation containing 10% indium, with traces of zinc, copper, and lead, was practically pure after ten crystallisations. A specimen of electrolytic gallium which contained a trace of zinc was purified by heating the metal in a current of dry hydrogen at a dull red heat, when the whole of the zinc sublimed. A series of photographs of arc spectra of gallium from various purifications is given in the paper, together with a list of wave-lengths. J. F. S.

The Formation of Cobalt Aluminate, Cobalt Orthostannate, and Rinman's Green. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **96**, 71—74. Compare A., 1915, ii, 636).—The temperature at which cobaltous oxide begins to react with the oxides of aluminium, tin, and zinc varies with the rate at which the mixture has been heated previously, being higher the slower the heating. Dense cobaltous oxide, prepared from the nitrate, gives a higher temperature of reaction than the lighter oxide prepared from the carbonate. For the aluminate, the temperature ranges from 925° to 1025°, but in presence of potassium chloride it may be as low as 776°. The temperature for cobalt and tin oxides is from 1000° to 1075°, not being lowered by potassium chloride. Cobalt and zinc oxides react at 790—800°. C. H. D.

Iso- and Hetero-poly-acids. XIII. The Constitution of the Polymolybdates, Polytungstates and Polyvanadates. ARTHUR ROSENHEIM [and in part MARIANNE PIECK and JACOB PINSKER] (*Zeitsch. anorg. Chem.*, 1916, **96**, 139—181. Compare A., 1916, ii, 334).—The distinction between water of crystallisation and of constitution being difficult, the following method has been found useful. The salt is gently heated in a boat in a stream of carbon dioxide, and the loss of weight determined from time to time, the results being plotted. A series of isotherms may thus be obtained, by a comparison of which the dehydration may be studied and the point at which the compound begins to change in chemical properties observed.

Sodium paramolybdate has the composition

$$5Na_2O,12MoO_3,38H_2O.$$

The guanidinium salt has the composition

$$5(CH_6N_3)_2O,12MoO_3,4H_2O.$$

The following complex paramolybdates have been obtained: $(NH_4)_3H_7[CoMoO_4)_6],5H_2O$, $(NH_4)_4H_6[Cu(MoO_4)_6],5H_2O$,

$(NH_4)_3H_7[Mn(MoO_4)_6],3H_2O$,

$(NH_4)_3H_7[Mg(MoO_4)_6],6H_2O$, $(NH_4)_8[Sn(Mo_2O_7)_6],20H_2O$. All these compounds may be regarded as 6-molybdo-aquates,

$$R_5H_5[H_2(MoO_4)_6].$$

There are also numerous polymolybdates belonging to other series.

The alkali paratungstates contain $11H_2O$, but a potassium salt, $2K_2O,5WO_3,4H_2O$, has also been prepared. This may be free from water of crystallisation. The following salts are also described: $5ZnO,12WO_3,35H_2O$, $Na_3H_7[Ni(WO_4)_6],12H_2O$,

$$(NH_4)_3H_7[Ni(WO_4)_6],7{\cdot}5H_2O,$$

cobalt salts of varying composition, and

$$Na_3CuH_5[H_2(WO_4)_6],11{\cdot}5H_2O.$$

These may be regarded as 6-hexatungsto-aquates. A similar conclusion is reached in regard to the polyvanadates. C. H. D.

New Derivatives of Tungsten. J. BENNETT HILL (*J. Amer. Chem. Soc.*, 1916, **38**, 2383—2391).—By the action of sodium amalgam on tungsten hexachloride, a compound, $W_6Cl_{12},2HCl,9H_2O$, similar to the molybdenum compound, $Mo_3Cl_6,HCl,4H_2O$ (Rosenheim and Kohn, A., 1910, ii, 300), has been prepared. To prepare this compound, considerable quantities of tungsten hexachloride were required. This was obtained by the action of chlorine on finely divided tungsten in the presence of platinum-black, which is shown to be an extremely good catalyst for this reaction. A mixture of 15 grams of tungsten hexachloride and 105 grams of 3% sodium amalgam was mixed in an ice-cold mortar, placed in a Jena tube, which was closed at one end, and the tube exhausted. The reaction immediately took place, and was very violent. After heating just to redness, and immediately cooling, the contents of the tube were extracted with hydrochloric acid (D 1·08) and filtered, when an intense brown solution was obtained. On extracting this solution with ether, a yellow solution was obtained, which deposited crystals of the above composition. It forms pale yellow, shining needles, which are soluble in alcohol, acetone, acetic acid, and alcohol–ether mixtures, but almost insoluble in anhydrous ether. It dissolved in water, and the solution, on keeping, deposited a yellow compound and then a black compound, both being products of hydrolysis. Potassium hydroxide added to the solution gave a clear yellow solution, which rapidly darkened, and from which weak acids precipitated a black, gelatinous precipitate of hydrated W_2O_3. The brown alkaline solution, on keeping for twenty-four hours in the air, slowly loses its colour, and when treated with weak acids yields a yellow, gelatinous precipitate of hydrated WO_2. J. F. S.

Reduction of Vanadic Acid by Hydriodic Acid. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1916, **38**, 2369—2377).—Ditz and Bardach (A., 1916, ii, 347) have stated that vanadic acid is reduced by hydriodic acid to vanadium trioxide, according to the equation $V_2O_5+4HI=V_2O_3+2H_2O+2I_2$. This conclusion is at variance with the results of many other workers, and in consequence the author has repeated the experiments of Ditz and Bardach in the

absence of air. The method adopted consists in placing the requisite amounts of a solution of sodium vanadate, concentrated hydrochloric acid, and a considerable volume of water in a large separating funnel, which is fitted with a second, small separating funnel and a side-tube. A current of hydrogen is passed through the solution for twenty minutes to remove air. Then a quantity of 5% potassium iodide solution is admitted to the mixture, and this is followed by 25 c.c. of carbon disulphide, and the whole mixture shaken from time to time for about an hour. The carbon disulphide solution of iodine is then run off, and a fresh quantity of 25 c.c. of carbon disulphide added, and the process repeated. The addition and removal of carbon disulphide are continued until it becomes impossible to extract any further iodine after several hours' keeping. The combined carbon disulphide solutions are then titrated with sodium thiosulphate solution. From the experimental results, it is seen that the reduction only proceeds to quadrivalent vanadium; further, the reduced vanadium solution is blue in colour, and not green, as it ought to be if the reduction proceeds to the tervalent vanadium derivative. The results of Ditz and Bardach are attributed to oxidation by air of hydriodic acid, and it is shown that this reaction is catalysed by vanadium pentoxide. The mechanism of the reactions between vanadic acid and the halogen hydracids, and the influence of various factors on the equilibrium, has been discussed. J. F. S.

Pure Bismuth. F. Mylius and E. Groschuff (*Zeitsch. anorg. Chem.*, 1916, **96**, 237—264).—The estimation of minute quantities of impurities in commercially pure bismuth presents special difficulties, as the oxide and sulphide precipitates, which are amorphous, retain other metals obstinately. The electrolytic method of separation also fails. The basic salts form amorphous precipitates, and the best method of separation is found to be the crystallisation of the normal nitrate from concentrated nitric acid. This is also suitable for the purification of bismuth. The nitrate, if already of fair purity, is dissolved in half its weight of 8% nitric acid and mixed with an equal weight of the concentrated acid. The crystals, which separate on cooling to 0° or −10°, are washed with a little ice-cold nitric acid. All impurities are thus concentrated in the mother liquor. The nitrate is converted into oxide by heat, and the oxide is then reduced by fusion with potassium cyanide. A further purification, if necessary, is effected by melting the metal under paraffin and removing the first (purest) crystals by means of a glass spoon.

For the analysis of nominally pure bismuth, 100 grams of the metal are dissolved in nitric acid free from chlorine. A first crop of crystals of nitrate is deposited on cooling, and two further crops may be obtained by evaporating the filtrate. The first and largest crop is redissolved in 8% nitric acid and filtered from tin oxide, if present. Addition of concentrated nitric acid then gives crystals of bismuth nitrate, which may be regarded as pure. The later crops are purified in the same manner, and the united filtrates will

yield further crops of colourless crystals, which, however, must be tested for lead, which separates with the crystals as soon as the lead amounts to 1% of the bismuth present.

The insoluble residue contains the tin, antimony, arsenic, gold, silver compounds, silicate slags, and carbon. The final mother liquor contains silver, copper, arsenic, nickel, and other metals. Various samples of bismuth sold as pure contain from 0·03 to 0·25% of impurities, Kahlbaum's bismuth of 1914 containing much less than 0·01%, copper (0·001) being the only impurity present in weighable quantity.

Purified bismuth melts at 271·0°, and when pressed into wire at 195° has a specific electrical resistance of 1·20. C. H. D.

The Action of Oxygen on Ruthenium. A GUTBIER, G. A. LEUCHS, H. WIESSMANN, and O. MAISCH (*Zeitsch. anorg. Chem.*, 1916, **96**, 182—206. Compare Gutbier and Ransohoff, A., 1905, ii, 534).—Finely powdered ruthenium oxidises rapidly when heated in oxygen, the maximum absorption of oxygen corresponding very closely with the formula RuO_2. The value actually obtained is very slightly lower, owing to volatilisation. It is independent of temperature between 700° and 1000°, although the rate of oxidation varies considerably. The formation of the volatile tetroxide begins at 600° and then increases rapidly, being 4000 times as great at 1200° as at 700°. Crystals of the dioxide are observed in the sublimate.

Metallic ruthenium is rendered more compact by heating at 800°. Previous heating at a high temperature in hydrogen reduces the velocity of oxidation. C. H. D.

Analytical Chemistry.

Modification of the Gravimetric Estimation of Chlorine and Silver. ERNST MURMANN (*Chem. Zentr.*, 1916, ii, 427; from *Osterr. Chem. Zeit.*, [ii], **19**, 115).—In the estimation of chlorine and silver the author recommends the reduction of the silver by addition of ash-free paper pulp before or after precipitation. After ignition of the filter and precipitate, the silver remains in the spongy, metallic condition, and can readily be tested for purity. Experiments show it to be free from silver chloride.

H. W.

Direct Estimation of Chlorine in Urine by the Modified Volhard's Method. A. HEIDUSCHKA (*Chem. Zentr.*, 1916, ii, 347; from *Apoth. Zeit.*, 1916, **31**, 279).—Repeated experiments have convinced the author of the necessity of removing proteins before performing the titration. H. W.

Separation of Hydrofluoric Acid and Hydrofluosilicic Acid. J. G. DINWIDDIE (*Amer. J. Sci.*, 1916, [iv], **42**, 421—430).—The author has investigated the various methods which have been suggested for the separation and analysis of a mixture of hydrofluoric acid and hydrofluosilicic acid. The methods due to Katz (A., 1904, ii, 442), Rose, Stolba, and Greef (A., 1913, ii, 975), as well as modifications suggested by the author, all give low values for hydrofluoric acid. J. F. S.

Reagents for Use in Gas Analysis. V. The Relative Advantages of the Use of Sodium and Potassium Hydroxides in the Preparation of Alkaline Pyrogallol. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1916, **8**, 999—1001. Compare A., 1916, ii, 262).—Mainly a reply to Shipley (A., 1916, ii, 571). Although the reagent prepared with sodium hydroxide is superior to that prepared with potassium hydroxide as regards specific absorption and cost of materials, it is inferior as regards the time required for complete absorption and the convenience of manipulation. W. P. S.

Registering Apparatus for the Estimation of Excess of Oxygen in Lead-Chamber Gases. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1916, **21**, 223—224).—The apparatus consists of an air-tight chamber of about 30 litres capacity containing a 10-litre varnished caoutchouc balloon filled with hydrogen. This balloon is suspended by a thread attached to a pivoted arm fixed outside the chamber. The gases from the lead chamber are aspirated into the chamber, and any change in the density causes the balloon to rise or fall, the movement being recorded by a registering device (a pen and a moving chart, or a photographic apparatus) connected with the other end of the pivoted arm. W. P. S.

Titration of Sulphuric Acid. C. R. GYZANDER (*Chem. News*, 1916, **114**, 260—261).—Attention is directed to errors which may be introduced when a sulphuric acid solution is titrated with an alkali solution which has been standardised with an indicator different from that used in the actual titration. A correction should be applied for temperature, when necessary.
W. P. S.

Estimation of Total Nitrogen. Accurate Method of Estimating Ammonia Volumetrically After Destruction of Organic Matter in the Presence of Mercury. ED. JUSTIN-MUELLER (*Chem. Zentr.*, 1916, ii, 520—521; from *Bull. Sci. Pharmacol.*, 1916, **23**, 167—169).—When organic substances are destroyed in the presence of mercury according to Kjeldahl's method, a portion of the ammonia remains combined in the form of mercury ammonium compounds, and is not estimated by the method of Ronchèse. Low results are also obtained after addition of sodium sulphide or hypophosphite, but, according to the author, the results are accurate when potassium arsenite is used to decompose

the mercury–ammonium compounds. The estimation is performed in the following manner: urine (10 c.c.) is heated with concentrated sulphuric acid (5 c.c.) and mercury (*ca.* 0·1 gram). If the urine contains sugar the quantity of acid is increased in the ratio of 10% of the sugar content. As soon as the solution becomes colourless, the heating is discontinued, the solution cooled, and diluted to 50 c.c. with water. Five c.c. of the dilute solution are mixed with 10 c.c. of the arsenite solution and 5 drops of phenolphthalein, and neutralised by sodium hydroxide (10%); the precipitate is allowed to settle for a few seconds, filtered, the residue washed three times with water, and the ammonia estimated in the filtrate by the formaldehyde method of Ronchèse. The potassium arsenite solution is prepared by dissolving arsenious oxide (5 grams) with the help of potassium hydroxide (11·20 grams) or *N*-potassium hydroxide (200 c.c.) and making up the solution with water to 1000 c.c. H. W.

The Efficiency of the Aeration Method for Distilling Ammonia; in Answer to certain Criticisms. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1916, **38**, 2568—2572).—Polemical. A reply to Falk (compare A., 1916, i, 439; ii, 341). W. G.

The Boric Acid Method of Estimating Ammonia. LUDWIG ADLER (*Chem. Zentr.*, 1916, ii, 601; from *Zeitsch. ges. Brauwesen*, 1916, **39**, 162—164, 169—172).—The author has investigated the applicability of Winkler's method of estimating ammonia (A., 1913, ii, 527; 1915, ii, 172) in brewers' laboratories. The following precautions ensure good results: 50 c.c. of boric acid solution (40 grams of the crystalline acid in 1000 c.c. of water) are placed in the receiver, and the ammonia is led as deeply as possible into this solution during the first fifteen minutes of the distillation. Evolution of ammonia is complete in twenty minutes. It is necessary to use cooling during the distillation, so that the distillate passes into the receiver at the laboratory temperature. The ammonia is titrated with *N*/4- or *N*/10-sulphuric acid in the presence of methyl-orange. A control solution should be used [water (250 c.c.), a few drops of methyl-orange (0·5%), and *N*/10-sulphuric acid (0·15 c.c.) or the equivalent quantity of *N*/4-acid].

The absorptive capacity of boric acid for ammonia is increased by addition of glycerol. H. W.

Application of the Nitrometer for the Determination of Constitution and Estimation of Nitrogen in a Class of Nitro-compounds (Nitroamines). W. C. COPE and J. BARAB (*J. Amer. Chem. Soc.*, 1916, **38**, 2552—2558).—Using the decomposition flask method of Berl and Jurrissen (compare A., 1910, ii, 240, 242), the nitrometer method can be used for the estimation of nitric nitrogen in nitro-compounds where the nitro-group is attached to carbon through nitrogen. It can also be used

for nitroso-compounds of the type of nitrosodiphenylamine, where the nitroso-group is linked to carbon through nitrogen. Other nitroso-compounds of the type of *p*-nitrosodimethylaniline cannot be examined by this method. The nitrates of carbamide and guanidine cannot be estimated in the nitrometer in the usual way. They must first be converted into their respective nitro-compounds, after which they may be readily estimated. W. G.

Estimation of Nitric Nitrogen. F. M. SCALES (*J. Biol. Chem.*, 1916, **27**, 327—337).—The solution containing the nitrate is treated with alumina cream and then boiled with a little magnesia in the presence of a zinc–copper couple. In these circumstances the nitrate is quantitatively converted into ammonia, which distils over into a known volume of standard acid. A simple distilling apparatus suitable for the estimation is described. H. W. B.

Estimation of Amino-nitrogen in Urines containing Dextrose and Albumin. DONALD D. VAN SLYKE (*Proc. Soc. Expt. Biol. Med., New York*, 1916, **13**, 63; from *Physiol. Abstr.*, 1916, **1**, 41).—Albumin is best removed by adsorption on colloidal aluminium hydroxide (Welker); but if much is present it is best to coagulate it first by heat and acetic acid. Urea is removed by urease, but if dextrose is present, it combines with some of the ammonia liberated, and some amino-acid condenses with the dextrose. During urease action, therefore, the urine should be kept acid by adding three or four volumes of water charged with carbon dioxide. Dextrose is then removed by adding copper sulphate; this unites with the sugar and is precipitated by calcium hydroxide. The alkaline filtrate is concentrated in a vacuum; this removes ammonia, and free amino-nitrogen can then be estimated. If albumin is present in diabetic urine this treatment removes the albumin also. G. B.

Use of Uranium in Analyis. J. C. THOMLINSON (*Chem. News*, 1916, **114**, 239).—Potassium ferrocyanide is untrustworthy as an indicator in the estimation of phosphoric acid by titration with uranium acetate solution. W. P. S.

Method of Extraction as Affecting the Estimation of Phosphoric Acid in Soils. HARRISON HALE and W. L. HARTLEY (*J. Ind. Eng. Chem.*, 1916, **8**, 1028—1029).—The authors confirm Brauer's statement (A., 1915, ii, 66) that as much phosphoric acid is extracted from a soil by a two hours' digestion with $2N$-nitric acid as is obtained by a ten hours' digestion with hydrochloric acid (D 1·115); hydrochloric acid also extracts substances from the soil which interfere with the estimation of the phosphoric acid. W. P. S.

Removal of Phosphoric Acid in Qualitative Analysis. LUDWIG GATTERMANN and HANS SCHINDHELM (*Ber.*, 1916, **49**, 2416—2422).—The removal of phosphoric acid by the use of tin was regarded as being due to the formation of stannic phosphate until recent years, when Mecklenburg (A., 1913, ii, 529) advanced

the theory that the phosphoric acid was merely adsorbed by the stannic acid, and introduced the idea of using a stannic acid gel instead of metallic tin. Both processes have the disadvantages that the solutions must be as free as possible from hydrochloric acid and that the quantity of tin required is enormous, being about 20 grams of SnO_2 for 0·5 gram of phosphoric acid.

It is now found that a *freshly prepared, cold* solution of crystalline stannic chloride is an excellent agent for removing phosphoric acid, even in hydrochloric acid solutions. Stannic phosphate is precipitated on boiling, in a form which is easily filtered at the pump, the amount of the agent necessary for 0·5 gram being only 2 grams, that is, 1 gram of SnO_2. In a test case, only 0·06% of phosphoric acid was left unprecipitated.

In order to find whether the metals of the ammonium sulphide or carbonate groups are carried down with the precipitate, solutions containing 0·5 gram of phosphoric acid and 5 mg. of the cations were treated with the stannic chloride solution. Chromium and iron are carried down to a certain extent, but all the other metals can be detected with ease in the clear filtrate.

The chief difficulty in applying the method occurs when the amount of phosphoric acid to be removed is small and unknown. An excess of stannic chloride must be used, but if the amount of stannic phosphate is small the stannic acid will not be precipitated in a filterable condition. It becomes necessary then to add phosphoric acid. The following procedure is recommended for the inexperienced worker: starting with 1 gram of substance, the solution from the hydrogen sulphide group is concentrated to 100 c.c., mixed with 5 c.c. of 6% ammonium phosphate, nearly neutralised, acidified with 3 c.c. of 7—8% hydrochloric acid, boiled, and mixed with 3 c.c. of the stannic chloride solution containing one part of the hydrate to one of water. Some of the mixture is filtered and tested with ammonium molybdate, and then the stannic chloride is added 0·5—1 c.c. at a time until succeeding filtrates contain no phosphoric acid. The whole quantity is finally filtered, excess of tin is removed by means of hydrogen sulphide, and the further tests are then proceeded with. The experienced worker is able to judge very largely by the intensity of the molybdate precipitate given by the original substance how much stannic chloride to use. J. C. W.

The Estimation of the Adsorption Capacity of Animal Charcoal. GEORG JOACHIMAGLU (*Biochem. Zeitsch.*, 1916, **77**, 1—13).—A method is given for estimating the adsorption capacity of charcoal by means of iodine solution. A charcoal should have such adsorptive capacity that 0·1 gram takes up at least the iodine equivalent of 10 c.c. of a $N/10$-solution. Those charcoals which have the greatest power of adsorbing iodine also adsorb the largest amounts of methylene-blue and tetanus toxin. When iodine adsorbed on charcoal is administered to the human subject, as much is resorbed in the system as if it had been applied free.

S. B. S.

A New Tube for Soda-Lime. A New Absorbent for Carbon Dioxide in Steel Analysis. G. L. KELLEY (*J. Ind. Eng. Chem.*, 1916, **8**, 1038—1039).—The soda-lime tube described consists of a vertical glass tube 5 inches in height and 1 inch in diameter; it has a neck at the top, and a flat base 1·5 inches in diameter. A capillary inlet is sealed into the side of the tube at a height of 2 inches, the portion of the capillary inside the tube being bent downwards so that it reaches nearly to the bottom of the tube. A layer of cotton-wool is placed at the base of the tube; this is covered with granular calcium chloride, a thin layer of cotton-wool is placed on the latter, and the tube is then filled with soda-lime.

An absorbent, which has about four times the efficiency of soda-lime, is prepared by dissolving 500 grams of sodium hydroxide in 500 c.c. of water, then adding 1000 grams of sodium hydroxide, and stirring in shredded asbestos until the mixture no longer appears capable of wetting more asbestos. The mixture is now heated at 180° for four hours, more asbestos being added gradually, cooled, and ground to pass a 10-mesh sieve. W. P. S.

Separation of Lithium from the other Alkali Metals. SAMUEL PALKIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2326—2332).—The author describes a method for the quantitative separation of lithium from sodium and potassium. Working with about half a gram of the mixed salts, which must be converted into chlorides, the mixture is dissolved in the minimum quantity of water (about 1·5 c.c.), one drop of concentrated hydrochloric acid is added, and then 20 c.c. of absolute alcohol are added drop by drop; this is followed by 60 c.c. of ether (D 0·717). The mixture is left for five minutes and then filtered through a Gooch crucible. The precipitate is well washed with a mixture of 1 part of alcohol and 4—5 of ether. The filtrate is evaporated to dryness, dissolved in 10 c.c. of absolute alcohol, and treated with 50 c.c. of ether and 1 drop of hydrochloric acid, and kept for thirty minutes. It is then filtered through the same Gooch crucible. The filtrate now contains practically nothing but lithium chloride, which is converted into sulphate and weighed in the usual manner. A large number of analyses of mixtures are given, from which it is clear that the method is both rapid and accurate. J. F. S.

Estimation of Manganese in Steel. J. A. CASHMORE (*Chem. News*, 1916, **114**, 239).—Two grams of the sample are dissolved in hydrochloric acid, the solution is treated with a small quantity of potassium chlorate, then evaporated to expel free chlorine, and diluted to about 400 c.c. Zinc oxide suspended in water is now added in excess, the mixture is boiled for two minutes, the precipitate collected on a filter, and washed with hot water. A white precipitate of zinc hydroxide may form in the filtrate, but this is of no importance. The filtrate is heated at 60°, 1 gram of ammonium persulphate and an excess of ammonia are added, the mixture is boiled, and the precipitated

hydrated manganese dioxide is collected, washed, ignited, and weighed as Mn_3O_4. It is advisable to dissolve the ignited precipitate in hydrochloric acid and reprecipitate the manganese with ammonium persulphate and ammonia. W. P. S.

The Microchemical Detection of Iron, especially that contained in the "Masked" Form in Plants. ADELE WIENER (*Biochem. Zeitsch.*, 1916, **77**, 27—50).—The method of Macallum (A., 1895, ii, 518) for the setting free of masked iron by alcoholic solutions of mineral acids has been subjected to experimental investigation by the author, who fails to confirm Macallum's statements. Potassium ferrocyanide, when treated with alcoholic solutions of acids in vessels coated with paraffin, failed to give the iron reactions even after ten weeks. It is assumed that in Macallum's experiments the iron found was derived from the glass or the reagents used. In only a very small percentage of cases, furthermore, could iron be detected in plants after hardening the microscopic preparations with acidified alcohol, and attention is directed to the fact that ordinary alcohol of commerce is apt to contain traces of iron. The conclusion is drawn that no really satisfactory method exists for the microchemical detection of masked iron in plants. S. B. S.

Detection of Ferrous Salts in Body Fluids by means of the Phosphotungstic Reagent. ALIN POPESCO (*Chem. Zentr.*, 1916, ii, 427; from *Buletinul Chimie*, 1916, **18**, 3—6).—The author is led to the conclusion that the phosphotungstic reagent (Richaud and Bidot, A., 1909, ii, 350) is not specific for ferrous salts, since the reaction is also shown by other organic and inorganic oxidisable substances. Positive reactions were obtained with stannous chloride, sodium thiosulphate, ammonium sulphide, the alkali sulphides, uric acid, resorcinol, phloroglucinol, ninhydrin, tannin, etc. H. W.

Estimation of Basicity of Chromium Extracts and Infusions. W. APPELIUS and R. SCHMIDT (*Chem. Zentr.*, 1916, ii, 109; from *Collegium*, 1916, 161—164).—The chromium extract or infusion is so diluted that 1—1·5 grams Cr_2O_3 are present per litre. For the estimation of chromium, 50 c.c. of the solution are treated with sodium peroxide, boiled for ten minutes, treated with sulphuric acid, and again boiled for five minutes. The liquid (about 150 c.c.) is transferred to a stoppered flask, 10 c.c. of potassium iodide solution (10%) and 5 c.c. of dilute hydrochloric acid (1 in 4) are added, and, after twenty to thirty minutes, the titration is performed with thiosulphate solution. For the estimation of the copper value (acidity of the acid combined with chromium), 50 c.c. of the diluted solution are boiled for ten to fifteen minutes with copper oxide (0·5—1 gram); the solution is decanted, the residue twice boiled with a small quantity of water, filtered, and washed; the cooled filtrate is treated with 10 c.c. of potassium iodide solution (80:250) and titrated with thiosulphate

solution. When the dilute chromium solution is boiled with copper oxide, copper sulphate is formed and chromium precipitated; only about three-quarters of the acid combined with the chromium is transferred to the copper, but the relationship is almost absolutely constant in all cases. A simpler and possibly more accurate process consists in boiling 100 c.c. of the dilute chromium solution with copper oxide (1—2 grams), diluting to 200 c.c., allowing the precipitate to settle, and performing the estimation in 100 c.c. of the clear solution. The copper value is defined as the quantity of copper corresponding with 100 grams of chromium sesquioxide; the relationship between this value and the basicity is expressed in a table.

The process is valid for chromium sulphate, chloride, and formate, but not for the lactate. H. W.

Analysis of certain Tungsten Derivatives. ORLAND R. SWEENEY (*J. Amer. Chem. Soc.*, 1916, **38**, 2377—2383).—A method of analysis of arsenotungstates, antimoniotungstates, and vanadiotungstates is described. In the case of arsenotungstates, a quantity of the sample was placed in a glass tube open at both ends, and this placed in a combustion tube, which was connected with a receiver. The tube was heated at 200°, and a current of dry hydrogen chloride passed over for about an hour. The apparatus was then allowed to cool, the sample moistened with water, and the process repeated for thirty minutes more. This was repeated three times. The receiver was then changed, and the process repeated until the distillate in a fresh receiver contained no arsenic. When the whole of the arsenic had been removed, the contents of the combustion tube were washed into an evaporating dish with dilute ammonia, and evaporated to dryness on a water-bath. The residue was digested with 1:1 nitric acid in the usual way. The residue then consisted of tungsten trioxide and sodium nitrate. This was dissolved in sodium hydroxide, precipitated with mercurous nitrate, and the tungsten weighed as the trioxide. In the case of vanadiotungstates, the same method was employed, but it was found that after a time the material was no longer attacked, although a considerable quantity of vanadium was still present. Consequently, at this point a mixture of chlorine and hydrogen chloride was substituted for the hydrogen chloride, when the whole of the vanadium rapidly distilled over as the reddish-brown oxychloride. The tungsten was estimated as before. The vanadium was estimated by reduction to the vanadyl salt with sulphur dioxide and titration with standard potassium permanganate. The author describes a piece of apparatus in which the separation of the vanadium and tungsten is conveniently carried out. In the case of antimoniotungstates, the same procedure is adopted as in the case of arsenotungstates. Typical analyses in all three cases show that fairly concordant results may be obtained. The author describes two derivatives of bismuthotungstic acid. The sodium, ammonium, and potassium salts of this acid, of the type $3M'_2O,2Bi_2O_3,11WO_3,xH_2O$, were

described by Smith and Balke (A., 1904, ii, 179). By treating the potassium salt with a mercurous salt, the author has isolated the compound, $3Hg_2O,2Bi_2O_3,11WO_3,15H_2O$, as a yellow, well-defined, and stable substance. A quantity of this substance was covered with water and a quantity of hydrochloric acid, insufficient completely to decompose it, added. The mixture was kept for several hours and filtered, and the filtrate evaporated at a low temperature under reduced pressure, when a green oil appeared. This was dried in a desiccator over sodium hydroxide until the odour of hydrogen chloride was no longer evident, when a greenish-yellow solid of the formula $2Bi_2O_3,6HCl,11WO_3$ was obtained.

J. F. S.

The Volumetric Estimation of Tin. R. L. HALLETT (*J. Soc. Chem. Ind.*, 1916, **35**, 1087—1089).—The methods in common use for the volumetric estimation of tin are critically reviewed, and the means of bringing the tin into a suitable solution discussed.

Stannous chloride solutions may be directly titrated with a solution of ferric chloride in hydrochloric acid; the presence of the chlorides of lead, zinc, aluminium, iron, cobalt, nickel, antimony, copper, and cadmium does not affect the titration except that the presence of a large amount of ferrous chloride retards the finish and lessens the delicacy of the end-point. Bismuth and mercury must be removed. As metallic antimony, copper, and arsenic and tungstic oxide would be precipitated during the reduction of the tin, and would be attacked by hot ferric chloride in acid solution, they must also be removed.

The direct titration of stannous chloride with potassium dichromate or permanganate gives correct results if the tin is completely in the stannous state and no other oxidisable substance is present, but the utility of the method is limited.

The titration of stannous chloride in cold hydrochloric acid solution with standard iodine affords a simple, short, and accurate process for the volumetric estimation of tin. The latter is brought into solution as the chloride and reduced by iron, nickel, aluminium, or antimony. Reduction and titration are best performed in an atmosphere of carbon dioxide in a solution containing not less than 25%, nor more than 40%, by volume of free, concentrated hydrochloric acid; the temperature of the solution to be titrated should not exceed 22°. The sample (0·5 to 2 grams) is brought into hydrochloric acid solution; sufficient concentrated hydrochloric acid is added to make a total of 50 c.c. of concentrated hydrochloric acid, and the solution heated at gentle boiling with a coil of nickel foil for thirty minutes, after any iron which may be present has been reduced. The solution is cooled in an atmosphere of carbon dioxide, the nickel foil removed, and washed with hydrochloric acid (1 in 3). Starch solution is added, and the solution titrated with iodine. Few of the elements ordinarily found in materials to be analysed for tin interfere with this method unless present in so large amount that their colour masks

that of the indicator. If antimony is present in quantity of more than 0·1 gram, it will be precipitated in a slimy condition during reduction, but this may be prevented by using a more strongly acid solution (75 c.c. acid instead of 50 c.c.). Copper in quantity of less than 0·05 gram does not interfere, but larger amounts must be removed. Bismuth and tungsten may be disregarded unless present in large amount. Titanium should be removed if present in quantity. Neither bismuth, tungsten, nor titanium in the amounts generally encountered affects the titration, particularly if the latter is performed rapidly; slow and careful titration appears to accelerate their reaction and gives them time to affect the results seriously. An estimation of tin may be accomplished by this method in about one and a-half hours, and the results are accurate to about 0·1%. H. W.

Application of the Method of Constant Boiling Point Mixtures to the Qualitative Analysis of certain Mixed Organic Liquids. W. R. G. Atkins (*Analyst*, 1916, **41**, 334—335).—The identification of a liquid by a determination of its boiling point is possible only when the liquid can be purified previously, and in dealing with small quantities of liquid such purification is frequently a difficult matter. It often happens, however, that another liquid may be added with which the unknown liquid will form a mixture of constant boiling point, so that the latter liquid may be identified in this way; a list of such mixtures, their boiling points, and compositions may be found in Young's "Fractional Distillation," etc. For example, benzene was added to a liquid smelling of alcohol, and the mixture was distilled. The temperature remained constant at 58·35° (the b. p. of the binary mixture of methyl alcohol and benzene) for a short time, thus indicating the presence of methyl alcohol; there were other halts at 64·8°, 68·25°, and 78·3° respectively, these being the boiling points of the mixtures ethyl alcohol–water–benzene, ethyl alcohol–benzene, and ethyl alcohol. The liquid therefore consisted of a mixture of methyl and ethyl alcohols with a trace of water. Other instances are given of the application of the method. W. P. S.

An Accurate Aeration Method for the Estimation of Alcohol in Fermentation Mixtures. Arthur W. Dox and A. R. Lamb (*J. Amer. Chem. Soc.*, 1916, **38**, 2561—2568).—The alcohol solution is saturated with ammonium sulphate, and the alcohol carried over by a current of air at the ordinary temperature into two cylinders of concentrated sulphuric acid, in which it is absorbed. The air is drawn through at the rate of 25 litres per hour, and the aeration is complete in eight to ten hours. The alcohol–sulphuric acid mixture is mixed with 10—15 grams of potassium dichromate in a distillation flask, the cylinders being rinsed with water free from carbon dioxide. The mixture is left for fifteen minutes and then distilled over a free flame, the liquid in the distilling flask being diluted from time to time with water

free from carbon dioxide. The results are accurate to within 1·5%. The volatile fatty acids in the original fermented liquid are not carried over in the aeration process. Acetone, although carried over, is not oxidised under the above conditions. Esters, particularly ethyl acetate, interfere with the estimation of alcohol by this method, but they may be determined separately. Aldehydes generally only occur in small quantities in fermentation mixtures, and are not likely to cause any appreciable error. Methyl alcohol under the above conditions is almost completely oxidised to carbon dioxide and water. The presence of toluene does not affect the accuracy of the method. W. G.

Differentation of the Two Naphthols by the Titanic Acid–Sulphuric Acid Reagent. G. Denigès (*Ann. Chim. anal.*, 1916, **21**, 216—217).—An intense green coloration is obtained when a small quantity of α-naphthol is mixed with a solution of titanic acid in concentrated sulphuric acid (compare A., 1916, ii, 544), whilst β-naphthol gives a blood-red coloration with the reagent. If the mixtures are diluted with acetic acid, the green coloration in the case of α-naphthol changes to reddish-violet, but the red coloration given by β-naphthol remains unaltered. If desired, the naphthol may be dissolved previously in acetic acid and the solution poured on the surface of the reagent; under these conditions, α-naphthol gives a green ring at the junction of the two liquids, and a reddish-violet coloured zone appears above the green ring; with β-naphthol, a red-coloured ring develops. These distinctive reactions are also given by the esters of the two naphthols.
W. P. S.

The Colours produced by Resorcinol in Solutions of certain Salts and the Use of these Colours as a means of detecting Resorcinol in the presence of other Phenols. Francis C. Krauskopf and George Ritter (*J. Amer. Chem. Soc.*, 1916, **38**, 2182—2187).—Resorcinol in an ammoniacal solution has been found to give a blue colour with zinc salts (compare Cerdan and de la Puente, *Anal. fis. quim.*, 1913, **2**, 98). Similar colour reactions are given with cobalt salts (violet), nickel salts (bluish-violet), and cadmium salts (blue). Cobalt salts give the most intense colour, and it has been tried to apply this as a test for the presence of resorcinol. The colour is the same in shade and depth whether cobalt chloride, nitrate, or sulphate is used, and it is sufficient to use 1 c.c. of the solution of the cobalt salt, containing 0·4 gram of cobalt per litre, for 50 c.c. of the ammoniacal resorcinol solution. Four c.c. of ammonium hydroxide solution (D 0·90) should be used, and 1 c.c. of a 1% resorcinol solution in 50 c.c. is sufficient to give an intense coloration. The colour takes longer to appear in the absence of air than if air is present, but once formed it is permanent. In contact with air the colour slowly changes to dull green and brownish-black. Under the above conditions the presence of other phenols, such as phenol, pyrogallol, quinol, and catechol, either mask or prevent the formation of the colour due to resorcinol.

By reducing the amount of ammonium hydroxide used to 0·3 c.c. and adding 3 c.c. of alcohol, a deep green colour was obtained with resorcinol, the formation of which was not hindered or masked by the presence of the other phenols. It was possible to detect in 50 c.c. of solution 0·10 gram of resorcinol in the presence of 0·2 gram of quinol or pyrogallol and 0·3 gram of phenol. W. G.

Clinical Methods of Estimation of Sugar in Blood. HARRY RAINY and CHRISTINA M. HAWICK (*Proc. Roy. Soc. Edin.*, 1915–1916, **38**, 186—191).—Bang's micro-chemical method (A., 1913, ii, 446) possesses advantages over several other methods, including those described by Gardner and MacLean (A., 1914, ii, 783), Stein and Wiseley, and MacLean (A., 1916, ii, 613). The quantity of blood required in Bang's method is very small, there is no difficulty about filtration, and the method may also be applied to the estimation of sugar in urine. The authors prefer to soak up the blood on a filter-paper which has been weighed previously in a weighing bottle, and to re-weigh the filter-paper plus blood; an ordinary balance is used in place of the torsion balance mentioned by Bang. Attention is directed to the necessity of boiling all the reagents before use in order to expel dissolved air.
W. P. S.

Estimation of Sugar in Meat Products, particularly Extracts. W. B. SMITH (*J. Ind. Eng. Chem.*, 1916, **8**, 1024—1027).—The removal of proteins, etc., from meat extracts, previous to the estimation of sugar by Fehling's method, is best attained by treatment with picric and phosphotungstic acids, followed by the addition of a minimum quantity of hydrochloric acid. Five grams of meat extract are dissolved in 25 c.c. of water, 4 grams of picric acid and about 50 c.c. of 20% phosphotungstic acid are added, the mixture is diluted to 100 c.c., filtered, 60 c.c. of the filtrate are treated with 3 c.c. of concentrated hydrochloric acid and 3 c.c. of water, again filtered, and the reducing sugars are estimated in this filtrate before and after inversion. W. P. S.

Estimation of Lævulose in Presence of Dextrose. L. LOEWE (*Proc. Soc. Exper. Biol. and Med., New York*, 1916, **13**, 71—72; from *Physiol. Abstr.*, 1916, **1**, 79).—The method depends on the yellow coloration developed after boiling and addition of a 0·2% solution of orcein and a 85% solution of phosphoric acid; the yellow colour becomes orange on addition of alkali. The test is made quantitative by colorimetric comparison with a standard lævulose solution treated with the reagents. Lævulose was detected in 1 c.c. of a 0·05% solution. Sucrose interferes, owing to hydrolysis by the acid. G. B.

Availability of certain Indicators in the Estimation of Gastric Acidity. C. C. FOWLER, OLAF BERGEIM and S. B. HAWK (*Proc. Soc. Expt. Biol. Med., New York*, 1916, **13**, 58; from *Physiol. Abstr.*, 1916, **1**, 40).—A comparative study of certain

indicators used in titration of the gastric juice showed that phenolphthalein is most satisfactory for estimating the total acidity, whilst the iodometric method is most useful in estimating the free acidity. Colorimetric determinations of the H ion concentration are inaccurate when applied to the gastric contents. G. B.

Duclaux's Method for the Estimation of Volatile Fatty Acids. F. W. J. BOEKHOUT and J. J. OTT DE VRIES (*Centr. Bakt. Par.*, 1916, ii, **46**, 505—513).—The authors have investigated Duclaux's method (A., 1896, ii, 504), and confirm the figures given in his tables for formic, acetic, and propionic acids; in the case of butyric and valeric acids, the results obtained were somewhat different from those recorded by Duclaux. It is shown that if the differences between the quantities of acid found in each successive fraction of the distillate are calculated into percentages of the acid remaining in the flask at the commencement of the distillation of each fraction (this quantity of residual acid being first calculated into 110 c.c. of the solution), a constant number is obtained for each fraction and is the same for each individual acid. This number is 3·5 for formic acid, 5·9 for acetic acid, 11·8 for propionic acid, 19·1 for butyric acid, and 26·0 for valeric acid. The application of the method to the analysis of mixtures of the acids is described.
W. P. S.

Estimation of Stearic Acid in Butter Fat. E. B. HOLLAND, J. C. REED, and J. B. BUCKLEY, jun. (*Chem. Zentr.*, 1916, ii, 350; from *J. Agric. Res.*, 1916, **6**, 101—113).—The experiments were performed according to the method of Hehner and Mitchell, which depends on the fact that when a mixture of fatty acids is dissolved in a solvent saturated at a definite temperature with the acid to be estimated and the solution is then cooled to this temperature, the desired acid is completely precipitated, provided that its solubility is not increased by the presence of other acids. A known weight of mixed fatty acids was warmed with a saturated solution of stearic acid in alcohol (95·25%) until a clear solution was obtained; this was cooled overnight in ice, gently shaken, and, after some time, the mother liquor was decanted as completely as possible. The residue was dissolved in ether, and, after removal of the solvent, dried at 100° and weighed. A series of blank experiments was also performed, since the precipitates retain quantities of mother liquor varying with their weights.

The proportion of stearic acid in the insoluble fatty acids from butter varied from 6·93 to 22·33%, according to the type of fodder and probably also to the individuality and period of lactation. Parallel experiments with beef tallow and palm oil showed a stearic acid content of 30·57% and 31·40% with the former, 8·91% with the latter. H. W.

Modification of Gerhardt's Test for Acetoacetic Acid in Urine. JACOB ROSENBLOOM (*Biochem. Bull.*, 1916, **5**, 25; from *Physiol. Abstr.*, 1916, **1**, 41).—The test is best carried out as

a contact test; 5 c.c. of the urine are poured on top of some 10% ferric chloride solution, and the port-wine colour appears in the zone of contact if acetoacetic acid is present. G. B.

The Estimation of β-Hydroxybutyric Acid in Urine. ERIK OHLSSON (*Biochem. Zeitsch.*, 1916, **77**, 232—240).—To 200 c.c. of urine are added 100 grams of ammonium sulphate and 25 c.c. of 20% sulphuric acid. Of the filtrate from this mixture, 275 c.c. are shaken with an equal volume of ethyl acetate in a separating funnel. The ethyl acetate is then transferred to another separating funnel and shaken with 25 c.c. of 30% sodium carbonate solution. The ethyl acetate is then transferred back to the first separating funnel and again shaken with the filtered urine and again transferred to the second funnel and shaken with the solution of sodium carbonate. These processes are repeated five times, and it is found that 93% of the hydroxybutyric acid is thus removed, and this can be estimated polarimetrically in the solution in sodium carbonate. For clinical purposes, a single extraction with ethyl acetate (and subsequent removal of the acid from this solution by sodium carbonate) will suffice. Under these conditions a nearly constant proportion of the hydroxybutyric acid (42%) is removed. S. B. S.

Modification of the Pratt Method for the Estimation of Citric Acid. J. J. WILLIAMSON (*J. Amer. Chem. Soc.*, 1916, **38**, 2193—2199).—A critical study of the various steps involved in Pratt's method for the estimation of citric acid (compare U.S.D.A. Bur. Chem., 1912, Circ. 88), as a result of which the author suggests certain modifications by means of which concordant results can be obtained.

In removing the citric acid from a plant juice, the author advises a medium of 30% instead of 50% alcohol (compare Jörgensen, A., 1907, ii, 312). The oxidation should be conducted so that the permanganate solution (0·5 gram per litre) enters at the rate of twenty to twenty-five drops in ten seconds, the distillate passing over at a slightly greater rate. Denigès's solution is added to the distillate at the rate of 15 c.c. for every 100 c.c. of distillate, the precipitate obtained by boiling being estimated volumetrically. The precipitate is dissolved in the least possible quantity of hot 5% hydrochloric acid, the solution cooled, very nearly neutralised with 10% sodium hydroxide solution, and made up to 100 c.c. An aliquot portion of this is poured into an excess of potassium iodide solution (28·0218 grams per litre), and the excess titrated back with a standard mercuric chloride solution. One c.c. of the potassium iodide solution is equivalent to 2·0 mg. of citric acid. W. G.

Detection of Picric Acid in Urine by the *iso*Purpurate Reaction. YDRAC (*Ann. Chim. anal.*, 1916, **21**, 225; from *Union Pharm.*, 1916, 337).—This reaction gives the most trust-

worthy results when carried out as follows. The urine is rendered slightly alkaline to litmus paper by the addition of a few drops of $N/10$-sodium hydroxide solution, potassium cyanide solution is then added, and the mixture heated at 60° to 70°; if picric acid is present, a red coloration develops after a few minutes. The test will detect the presence of as little as 0·025 gram of picric acid per litre of urine. Icteric urine does not give a coloration with the test, and albumin and biliary pigments do not interfere.

W. P. S.

Estimation of Hippuric Acid in Urine, Blood, Muscles, and Liver. HIIZU ITO (*J. Amer. Chem. Soc.*, 1916, **38**, 2188—2192).—The hippuric acid was converted into benzoic acid by boiling it with 25% sodium hydroxide for twelve hours, the solution then being acidified and extracted with light petroleum in a modified Soxhlet apparatus for extracting liquids, the petroleum being evaporated from the weighed extraction flask by a current of dry air, and the benzoic acid weighed. In the case of urine, any benzoic acid present was first removed by extraction before the hydrolysis. In the case of blood, it was defibrinated, and the protein and fat separated by heating it on a water-bath with dilute hydrochloric acid. In the case of muscle and liver, the material was finely shredded and extracted with hot water, the protein and fat removed as above from the filtrate, the filtrate being finally evaporated nearly to dryness and extracted with alcohol. After this treatment, the residue was hydrolysed and the estimation performed as above. W. G.

Colour Reactions of Aromatic Aldehydes. PETER POOTH (*Chem. Zentr.*, 1916, ii, 522; from *Schweiz. Apoth. Zeit.*, 1916, **54**, 377—382. Compare Häuszler, *Zeitsch. anal. Chem.*, 1913, **53**, 363, 691).—The condensation of aromatic aldehydes with sulphonated aromatic amino-compounds leads to the formation of characteristic, distinctly coloured azomethines, which can be employed in the identification of aldehydes. Aromatic aldehydes yield more distinct colorations with naphthionic than with sulphanilic acid; in most cases, the azomethine separates directly on cooling. The test is performed as follows: 3—4 c.c. of an aqueous solution of sodium sulphanilate or naphthionate (10%) are heated in a porcelain dish on the boiling-water bath; a boiling alcoholic solution of the aldehyde is added, which causes the appearance of a pale yellow to red coloration, and the solution is evaporated to dryness, the colour generally being deepened thereby. Before evaporation, a few drops of the solution are removed, diluted with water, cooled, and treated with a few drops of dilute sulphuric acid; in many cases the colour is deepened, in others completely changed. Certain of the reaction products, particularly those derived from nitro-aldehydes, are sensitive to daylight. The products obtained from substituted aldehydes are less stable.

The colorations given by the individual aldehydes are described and tabulated in the original paper. H. W.

Estimation of Vanillin in Vanilla Extract. ARTHUR W. DOX and G. P. PLAISANCE (*Amer. J. Pharm.*, 1916, **88**, 481—484). —Thiobarbituric acid may be used for the quantitative precipitation of vanillin. To estimate vanillin in vanilla extract, 25 c.c. of the sample are heated to expel alcohol, and then diluted to 50 c.c. with lead acetate solution. After a few hours, the mixture is filtered, 40 c.c. of the filtrate are treated with hydrochloric acid in quantity sufficient to make the acidity 12% and the volume 50 c.c., the lead chloride is separated by filtration, and 40 c.c. of this filtrate are mixed with thiobarbituric acid in 12% hydrochloric acid solution. The precipitate, which is the simple condensation product, 4-hydroxy-3-methoxybenzylidenemalonylthiocarbamide, is collected after eighteen hours, washed with 12% hydrochloric acid, then with water, dried at 98°, and weighed. Thiobarbituric acid is a general precipitant for aromatic aldehydes, and the method cannot be applied to artificial extracts which have been coloured with caramel, since the latter contains furfuraldehyde derivatives. The presence of caramel in an extract is indicated by the brown precipitate which forms when phloroglucinol is added to the clarified extract containing 12% of hydrochloric acid. W. P. S.

A Comparison of Barbituric Acid, Thiobarbituric Acid, and Malonylguanidine as Quantitative Precipitants for Furfuraldehyde. ARTHUR W. DOX and G. P. PLAISANCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2156—2164).—Of the three reagents tested, barbituric acid only gives a quantitative precipitation with furfuraldehyde in solution in 12% hydrochloric acid when a large excess (eight to sixteen times the theoretical quantity) of the barbituric acid is used (compare Unger and Jäger, A., 1903, ii, 187, 456). Thiobarbituric acid, on the other hand, gives a quantitative precipitation without any large excess being used, the results being if anything, slightly too high. The reaction is quantitative for such small amounts of furfuraldehyde as 12 mg. This reagent is preferable to phloroglucinol, since no correction for solubility of the precipitate is necessary. Furthermore, the precipitate is a definite compound, *furfurylidenemalonylthiocarbamide*, which is bright lemon-yellow in colour, very flocculent, and voluminous. It is easy to filter and wash. The thiobarbituric acid used must be quite pure and free from any cyanoacetic ester, or the results obtained will be too low. Like phloroglucinol, it also gives a precipitate with methylfurfuraldehyde.

The condensation of furfuraldehyde with malonylguanidine is not quantitative. W. G.

Estimation of Salol and Acetanilide in a Mixture of the two, and of Salol and Phenacetin in their Mixtures. BENEDICT SALKOVER (*Amer. J. Pharm.*, 1916, **88**, 484—485).—A method for the estimation of these substances when in the form of tablets and mixed with talc, starch, acacia, tragacanth, etc., depends on the insolubility of acetanilide and phenacetin in light

petroleum, and on the solubility of salol in this solvent. A weighed portion of the powdered tablets is shaken for thirty minutes in a closed flask with a measured quantity of chloroform; an aliquot portion of the chloroform solution is then filtered into a weighed flask, the chloroform is evaporated, the residue is dried at 60°, and weighed. It represents the salol and acetanilide, or salol and phenacetin, contained in the mixture. Another portion of the sample is now extracted in a similar way with light petroleum. The residue obtained when an aliquot portion of the solution is evaporated consists of salol, but its weight must be corrected for a small amount of acetanilide or phenacetin which is dissolved. One hundred c.c. of light petroleum (b. p. 40—45°) dissolve 0·015 gram of phenacetin or 0·022 gram of acetanilide.

W. P. S.

Bromine and Iodine Compounds of Hexamethylenetetramine (Urotropine). K. SUGIURA and K. G. FALK (*Biochem. Bull.*, 1916, **5**, 17—21; from *Physiol. Abstr.*, 1916, **1**, 65).—A method of estimation of this extensively used drug can be based on the formation of the tetraiodide.

G. B.

Estimation of Polypeptides and Amino-acids in Blood. J. AMANN (*Chem. Zentr.*, 1916, ii, 430—431; from *Schweiz. Apoth. Zeit.*, 1916, **54**, 309—313).—The following method is adapted for clinical purposes. Fresh, centrifuged blood serum (1 c.c.) is placed in a suitable dialyser which has been shown to be impermeable to albumin, but readily permeable to polypeptides, and, after addition of a few drops of toluene, dialysed for sixteen hours at 37° against sterilised water (10 c.c.) saturated with toluene. Five c.c. of the dialysed solution are mixed with ninhydrin solution (1%, 0·2 c.c.); on the other hand, 1 c.c. of a solution prepared by hydrolysing casein with sulphuric acid (25%) and containing 10 mg. N in 100 c.c., is diluted with water (4 c.c.) saturated with toluene, and ninhydrin solution (0·2 c.c.) is added. The two solutions are placed in the boiling-water bath for twenty minutes, cooled, and their colorations compared in the chromometer. With similar intensities, the concentration of amino-nitrogen is inversely proportional to the thickness of the layer. In the place of the standard solution described above, solutions of mixtures of methyl-violet, methylene-blue, and aniline-brown can be employed. When approximate values only are required, the chromometer can be dispensed with.

H. W.

General Conceptions of Intoxication. II. Protection against "Structure" Poisons; a Method for Biochemical Detection of small amounts of Substances. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **76**, 321—325. Compare A., 1916, i, 778).—Hæmolysis (or agglutination) of red blood corpuscles by mercuric chloride or copper sulphate can be prevented by the addition of the requisite amount of potassium cyanide. As only very small amounts of the reacting substances are employed, it is

suggested that these facts form a basis of a biochemical method for estimating small amounts of the cyanide. S. B. S.

The Content in Suprarenin [Adrenaline] in the Ordinary Commercial Preparations and the Methods of Estimation. FRITZ JOHANNESSOHN (*Biochem. Zeitsch.*, 1916, **76**, 377—391).—Adrenaline can be estimated colorimetrically by Folin's phosphotungstic reagent, and biologically by the perfusion method of Läwen and Trendelenburg when present by itself, but not in the presence of novocaine or alypin. When these substances are present, however, the colorimetric method of Fränkel, Allers, and Bayer can be used (iodic acid in the presence of sulphanilic acid) under conditions specified by the author. This method has been employed for estimating the adrenaline content of various commercial preparations and of the conditions under which these may be preserved without loss of the adrenaline. S. B. S.

Palpitation and Caffeine; Detection of Caffeine in Urine. A. CH. HOLLANDE and L. THÉVENON (*J. Pharm. Chim.*, 1916, [vii], **14**, 324—326).—Malingerers sometimes take a dose of 1 gram or more of caffeine before undergoing a medical examination, since this alkaloid increases the heart-beats up to 160 per minute. When such large doses are taken, caffeine is easily detected in the urine; the authors have isolated 0·26 gram of caffeine from 2 litres of urine passed by a man who had taken 1 gram of the alkaloid. In suspected cases the urine should be treated with 10% of its volume of basic lead acetate solution, filtered, the filtrate treated with sodium sulphate to precipitate excess of lead, and the solution then extracted with chloroform. A distinct, crystalline residue is obtained on evaporating the chloroform extract if caffeine is present, and the latter may be identified by the usual reactions. In the absence of caffeine, an amorphous residue remains when the chloroform solution is evaporated.
W. P. S.

A New Method for the Estimation of Nicotine in Tobacco. ALFRED TINGLE and ALLAN A. FERGUSON (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 27—31).—Based on results already given (A., 1916, i, 656), the authors have worked out a new method for the estimation of nicotine in tobacco. Into a 500 c.c. flask they place 20 grams of tobacco, 40 grams of barium hydroxide, and 150 c.c. of water, and distil the mixture with steam until the distillate gives no alkaline reaction with phenolphthalein. To the distillate 20 c.c. of sulphuric acid are added, and the liquid evaporated to about 50 c.c. This solution is made strongly alkaline with potassium hydroxide, a few drops of baryta water being added for clarification. The solution is then made up to 100 c.c., the precipitate allowed to settle, the supernatant liquid filtered, and its rotation then determined in the polarimeter. In a modification of the method, the nicotine is extracted from the steam distillate by chloroform. These two methods gave concordant results,

which were then compared with the results obtained, using the same specimen of tobacco, by the methods of Tóth and of Kissling. The latter processes give lower results than were obtained by the methods of the authors. T. S. PA.

Estimation of Strychnine in Nux Vomica. H. R. JENSEN (*Pharm. J.*, 1916, **97**, 458—461).—The hot (50°) nitration method prescribed in the British Pharmacopœia for the separation of strychnine from brucine yields low results; the deficiency in the amount of strychnine found may be from 5 to 11% of the quantity present. Nitration at 20° is recommended, provided that the nitric acid used is "active" or is "activated" by the addition of sodium nitrite. Attention is called to the fact that strychnine nitrate in an aqueous solution containing sulphuric and nitric acids is not readily decomposed when the solution is rendered alkaline; small quantities of strychnine nitrate are "salted out," and are extracted by the chloroform. The residue of alkaloid obtained when the solvent is evaporated should be weighed and then titrated; the difference between the two results indicates the quantity of strychnine nitrate present (the average quantity is 8·8% of the weight of the residue), and the true amount of alkaloid is obtained after applying this correction. W. P. S.

Chemical and Physiological Detection of several Alkaloids in the same Solution. EDUARDO PHILIPPI (*Chem. Zentr.*, 1916, ii, 604—605; from *Arch. Farmacol. sperim.*, 1916, **22**, 120—130).—The characteristic reaction of strychnine with sulphuric acid and potassium dichromate is not shown by 1 mg. of strychnine nitrate in the presence of 0·04 gram or more of quinine bisulphate, a transitory, garnet-red coloration being produced, which becomes green or greenish-grey; with smaller quantities of quinine, the reaction is distinct, but transient. The same effect is observed when salts of the alkaloids with the same acid or the free alkaloids are used. Crystals of strychnine picrate can be obtained in the presence of a large excess of quinine, but they are not then characteristic. The alkaloids are most simply and certainly separated by the use of sodium potassium tartrate; quinine tartrate is insoluble in solutions of alkali sulphates and tartrates, whereas the strychnine salt is soluble. Mixtures which do not give the characteristic reaction with potassium dichromate do not cause the characteristic symptoms in the frog. This effect is probablv not due to delayed absorption, but rather to a superposition of the symptoms of poisoning in which those predominate which are attributable to the alkaloid present in excess. H. W.

Volumetric Estimation of Indigotin. SAMUEL M. JONES and WALTER SPAANS (*J. Ind. Eng. Chem.*, 1916, **8**, 1001—1002).—The indigotin is sulphonated and then titrated with formaldehyde-sodium sulphoxylate. One gram of the powdered indigo (or 5 grams of a 20% paste) is heated at 60° for four hours with 30 c.c. of sulphuric acid (D 1·84); the mixture is then cooled, diluted

with water, again cooled, diluted to 1 litre, and filtered. Fifty c.c. of the filtrate are placed in a flask, 50 c.c. of 35% sodium hydrogen sulphite solution are added, a current of hydrogen is passed into the flask, the contents of the latter are heated at 75°, and titrated at this temperature with a 0·1% formaldehyde–sodium sulphoxylate solution. The flask should be closed with a cork through which pass inlet and outlet tubes for the hydrogen, a thermometer, and the nose of the burette. The formaldehyde–sodium sulphoxylate solution is standardised against pure indigotin under the conditions mentioned. W. P. S.

Indoxyl in Urine. ED. JUSTIN-MUELLER (*Chem. Zentr.*, 1916, ii, 242—243; from *Bull. Sci. Pharmacol.*, 1916, **23**, 85—92).—Maillard's hypothesis, according to which indigotin and indirubin are formed by polymerisation of hemi-indigotin pre-formed in urine, is criticised.

The following method is recommended for the detection of indoxyl in urine. About 10 c.c. of urine are treated with an equal volume of pure hydrochloric acid or half the volume of pure sulphuric acid; the solution is cooled and shaken with ether (2—3 c.c.). If the ethereal layer is not coloured, 2 to 4 drops of hydrogen peroxide (10%) are added, and the solution is again shaken, 2—3 drops of alcohol being added if an emulsion is formed. Addition of hydrogen peroxide is unnecessary if the characteristic coloration of the ether is produced by addition of the acid alone. In the presence of iodides and absence of indoxyl, the ether becomes yellow; if both are present, a green coloration is formed. Methylene-blue is not dissolved by ether.

Indoxyl is estimated in urine in the following manner: 50 c.c. of urine are purified by addition of lead acetate (4 c.c.) and so much crystalline sodium sulphate that the total volume is 55 c.c.; 11 c.c. of the filtered solution (=10 c.c. of the original urine) are mixed with pure hydrochloric acid (10 c.c.) and, if necessary, 2—5 drops of hydrogen peroxide (10 %). After being cooled, the solution is shaken with chloroform (3—5 c.c.), the chloroform layer removed, and the extraction repeated two or three times with such quantities of solvent that the total volume of the latter amounts to 9—10 c.c. The volume of the chloroform extract is made up to exactly 10 c.c., and the colour of the solution compared with that of a standard prepared by dissolving indigocarmine (0·89 gram) in boiling water (200—250 c.c.), addition of phenol (1 gram) to the filtered solution, and dilution to 500 c.c. It should be noted that the extracts have a rather more pronounced violet shade than the standard solutions.

Indigotin is formed by the condensation of two molecules of indoxyl, indirubin by the oxidation of indoxyl (1 mol.) to isatin, and condensation of the latter with one molecule of indoxyl. Indigotin and indirubin are thus both directly formed from the indoxyl in urine. Maillard's hypothesis of the existence of pre-formed indigotin may therefore be abandoned, as well as the supposition of the existence of two polymeric indigotins. H. W.

Microchemistry of Plants. XIV. Identification of Crocetin. O. TUNMANN (*Chem. Zentr.*, 1916, ii, 279; from *Apoth. Zeit.*, **31**, 237—238).—The investigation was undertaken with the object of discovering reactions by which crocetin can be distinguished from other carotinoids, particularly from carotin, and for this purpose powdered saffron was employed.

Coniine-crocetin, obtained by spreading the powder on a drop of water, addition of 1% coniine solution, and warming, is suitable for identification of crocetin. During drying, deep yellow, single, prismatic needles with direct extinction are formed. The microchemical preparations of the sodium and potassium compounds of crocetin cannot be accomplished by Decker's macrochemical method. The former is best obtained by boiling saffron powder for three to five minutes with 10% sodium carbonate solution; during drying, pale yellow nodules are formed, which become crystalline in a few days, the process being accelerated by addition of alcohol. The potassium compound is obtained by warming saffron powder with water and addition of alcoholic potassium hydroxide solution; a copper-red precipitate, consisting of fine drops, is first produced, which becomes powdery in the course of a few days, but never yields crystals. In addition, chrome-yellow, oily masses are formed, which within one to two hours become crystalline. The copper-red drops consist of carotin, the yellow crystals of potassium crocetin. The latter is readily soluble in water, which scarcely affects the carotin. Red drops only are formed in the pollen grains.

When the red solution of crocetin in dilute pyridine (1:1) is dried, reddish-brown, interlaced rhombs are produced, and crystallisation occurs in the course of a few days. The preparation of aniline-crocetin is readily accomplished, and forms the best method of identifying crocetin. Saffron powder is warmed for two to three minutes with aniline until bubbles commence to form; in the course of ten to twelve hours, numerous dark red nodules are formed, which dissolve slowly in alcohol and glycerol. If saffron powder is warmed with very dilute sodium hydroxide solution, treated with benzoyl chloride, and warmed until bubbles commence to form, fine, pale yellow and golden-yellow needles, grouped in tufts and clusters, are produced. H. W.

A Direct and Indirect Diazo-reaction for Bilirubin. A. A. HYMANS VAN DEN BERGH and P. MULLER (*Biochem. Zeitsch.*, 1916, **77**, 90—103).—The ordinary diazonium reaction for bilirubin as originally devised by Ehrlich was carried out in the presence of alcohol. It has been found by the authors that human bile yields the diazonium reaction in the absence of alcohol, and this they designate the "direct" reaction, in contradistinction to the "indirect" action, which is generally given by bilirubin in the presence of alcohol. They find that bilirubin ordinarily gives a colour with diazonium solutions in the presence of (1) methyl or ethyl alcohol; (2) salts of weak acids, such as cholic and citric acids; (3) when a trace of alkali has been added to the bilirubin solution. They have failed to discover what substance is present

in human bile which causes the "direct" action, that is, the colour reaction with diazonium solutions without addition of alcohol or the other substances mentioned above. They have applied the diazo-reaction to various sera, and find that horse-serum, which normally contains bilirubin, yields only the indirect action, as do also sera in which the presence of bilirubin is due to hæmolytic processes; on the other hand, sera of patients with jaundice due to obstruction give, at any rate in certain stages of the disease, a direct diazo-reaction. S. B. S.

Microchemistry of Æsculin and its Detection in Æsculus hippocastanum. O. TUNMANN (*Chem. Zentr.*, 1916, i, 1277—1278; from *Schweiz. Woch. Chem. Pharm.*, **54**, 45—47, 67—70).—Æsculin prepared from the bark of thin branches (thumb-thick) of *Æsculus hippocastanum* gathered in October crystallises from alcohol in large and small, flat prisms, m. p. 161°, the stellate or radiating groups of needles mentioned in the literature not being obtained.

For microchemical purposes the most suitable solvents are methyl alcohol and pyridine; from the latter æsculin separates in arborescent masses of needles. Dissolution of a crystal of æsculin in warm chlorine water is rapidly followed by the separation of a chloro-compound in shrub-like aggregates of filamentous, strongly polarising needles, which appear pale yellow in a thick layer. Dibromoæsculin, obtained by treating a saturated aqueous æsculin solution with potassium bromide solution containing 10% of dissolved bromine, separates as a flocculent precipitate, rapidly becoming crystalline. Gold chloride dissolves when heated in æsculin solution and gives rise after a short time to a deep blue, granular, crystalline precipitate. In sections, æsculin is best detected by means of the dibromo-derivative; the sections are left under a cover-glass in the reagent for some hours and are then cleared with aniline. T. H. P.

Detection of Ovalbumin in Urine. P. GODFRIN (*J. Pharm. Chim.*, 1916, [vii], **14**, 257—260).—Twenty-five c.c. of the urine are treated with 5 drops of glacial acetic acid and excess of sodium chloride; this treatment precipitates ordinary albumin, but not ovalbumin. After thirty minutes the mixture is filtered and the filtrate tested for the presence of ovalbumin, for which purpose Tanret's reagent is recommended. If the urine contains pseudo-albumins, the sodium chloride should be added thirty minutes after the addition of the acetic acid, and a further thirty minutes allowed to elapse before the mixture is filtered. W. P. S.

Criticism of the Method of Detecting Urinary Albumin by Heat; New Process permitting the Detection of the smallest traces of Albumin in Urine. P. GODFRIN (*J. Pharm. Chim.*, 1916, [vii], **14**, 294—303).—The author considers that by the usual method of acidifying the urine with acetic acid and saturating it with sodium chloride or sodium sulphate, an

error may arise due to the precipitation of pseudo-albumin. He recommends the following procedure. The reagent is a mixture of 90 c.c. of a cold saturated solution of sodium chloride and 10 c.c. of phosphoric acid (50%), the mixture being filtered. To 9 c.c. of the urine, acidified if necessary with dilute acetic acid and filtered, 1 c.c. of phosphoric acid (50%) is added, and the mixture filtered if necessary. Three to four c.c. of the filtrate are carefully run on to an equal volume of the above reagent, and the tube left for a time. The amount of albumin in the urine is indicated by the time taken for the formation of an opaque disk at the junction of the liquids, and also by the opacity of the ring. At the most, half an hour is sufficient for the formation of a nebulous ring indicative of the smallest traces of albumin in the urine. If uric acid separates during the test, it can be redissolved by plunging the test-tube into water at 50°, without mixing the layers. This method only precipitates albumin and primary albumoses, and the precipitate due to the latter disappears if the tube is plunged into water at 60°. W. G.

Rennin. HOWARD T. GRABER (*J. Ind. Eng. Chem.*, 1916, **8**, 909—910. Compare A., 1912, ii, 706).—There appears to be a seasonal variation in the rate at which milk is coagulated by rennin, the coagulation being more rapid, by some minutes, in the autumn and spring than in the summer and winter. In a method described previously for the assay of rennin (*loc. cit.*) the quantity of milk specified for use in the test was twice the volume intended. The corrected method is as follows: 0·4843 gram of the rennin is dissolved in 150 c.c. of water, and 10 c.c. of this solution are added to 1 quart of milk at 42°; the mixture is poured from one vessel to another three times and the time then observed when coagulation commences. Ten c.c. of the rennin solution with 1 quart of milk gives a proportion of 1:30,000, and the activity of the rennin used is reported as being 1:30,000 in the time required for the coagulation. W. P. S.

A Résumé of Tests for Pepsin. HOWARD T. GRABER (*J. Ind. Eng. Chem.*, 1916, **8**, 911. Compare A., 1912, ii, 706).—The albumin used in testing the strength of pepsin should be obtained from eggs which are from five to twelve days old, since with these eggs the amount of insoluble residue left after treatment with an active pepsin rarely exceeds 1 c.c. in volume. The volume of the residue also affords an indication of the age of the eggs used; a larger insoluble residue than usual shows that the eggs are quite fresh or more than twelve days old. If a second test after six days gives a smaller residue, the eggs were fresh, whilst an increased quantity of residue shows that the eggs were more than twelve days old. W. P. S.

General and Physical Chemistry.

The Spectra of Carbon and Hydrocarbon. CHARLES W. RAFFETY (*Phil. Mag.*, 1916, [vi], **32**, 546—559).—Photographs of the "Swan" spectrum obtained under varying conditions are discussed in detail. A new series of faint lines in the region of λ 4107—λ 4025 is described, together with some bands of unknown origin which are associated with the "Swan" spectrum.

H. M. D.

Regularities in the Spectra of Neon and Argon. K. W. MEISSNER (*Physikal. Zeitsch.*, 1916, **17**, 549—552).—Recent measurements of the wave-lengths of lines in the red portion of the neon spectrum show that all the more intense lines are members of groups of triplets or quadruplets characterised by the same wave-number differences. Similar quadruplets are found in the red region of the argon spectrum, but the groups are in many cases incomplete. H. M. D.

The Groups of Rays of Iron under the Selective Influence of Thermal and Chemical Actions. G. A. HEMSALECH (*Compt. rend.*, 1916, **163**, 757—759. Compare A., 1908, ii, 445).—The iron rays emitted by a Bunsen flame may be divided into three classes, namely: (1) Rays emitted by the exterior flame and strengthened in flames of higher temperature, being particularly sensitive to thermal actions. Examples are λ 3860, 3920, 4376. (2) Those rays emitted under the influence of chemical action; they are very marked in the cone but feeble in the flame. Examples are the triplets at λ 4046 and 4384. (3) This class includes the rays of the "supplementary" spectrum, that is, the rays of the cone proper. Examples, λ 3936, 4119, 4957. In each of these categories of spectra there are peculiar groups of rays, composed of three, four, or more rays. The groups of the first and second class converge towards the red and of the third class towards the violet. W. G.

Optical Investigations of the Constitution of Nitric Acid. KONR. SCHAEFER [with H. NIGGEMANN] (*Zeitsch. anorg. Chem.*, 1916, **97**, 285—311. Compare A., 1910, ii, 562).—Optically pure nitric acid up to $12N$ may be obtained by distilling the ordinary pure acid, D 1·4, over carbamide. More concentrated acid is obtained by distilling the ordinary acid, mixed with two or three volumes of sulphuric acid, in a vacuum apparatus consisting entirely of glass and protected from light.

The solutions are contained in vertical absorption vessels provided with plane parallel plates of silica, the inner tube being raised or lowered to vary the thickness of the absorbing layer. For high temperatures, the vessel is surrounded by an electrically heated copper block, and for low temperatures by a cooling coil and vacuum jacket.

Soluble nitrates exhibit selective absorption, whilst alkyl nitrates only cut off the ultra-violet end of the spectrum. Dilute nitric acid, from 0·02 to 1*N*, has a spectrum like that of the salts, but at 2*N* a transition to the ester type begins, and the concentrated acid has only continuous absorption. Solid and molten potassium nitrate have an absorption band in the same position as the solution. The difference between the two types of spectra is not attributable either to dissociation or to hydration, and can only be explained by a difference in the arrangement of the subsidiary valencies in the NO_3 group. C. H. D.

The Ultra-violet Absorption Spectra of Blood Sera. S. JUDD LEWIS (*Proc. Roy. Soc.*, 1916, [B], **89**, 327—335).—Quantitative measurements of the ultra-violet absorption of blood sera have been made by the use of a sector spectrophotometer in conjunction with a quartz spectrograph. The intensity of the absorption was determined by matching the absorption spectrum against normal spectra of known intensity, and the results are shown by a curve in which the extinction-coefficient is plotted against the wave-length of the ultra-violet radiation.

The absorption curve for normal serum shows a well-marked band with a maximum at about λ 2800, followed by a minimum at λ 2540, from which point the absorption curve rises steeply to a second maximum at about λ 2400. From a comparison of the curves for a large number of samples of normal serum, it appears that the section of the curve between the maximum at λ 2800 and the minimum at λ 2540 is the portion which is most subject to variation. The examination of pathological sera has also shown that this section of the curve is the region where the greatest differences are to be found. There is, moreover, distinct evidence in favour of the view that the minimum at λ 2540 is displaced appreciably under certain pathological conditions.

Since serum is a mixture of substances in somewhat variable proportions, the absorption curves represent the resultant of several superposed curves, each characteristic of some constituent of the serum. By separating the proteins from the non-proteins and comparing the spectra of the corresponding solutions, it has been found that the chief central band (maximum at λ 2800) is due almost entirely to proteins.

Some observations on horse serum and egg-albumin show that the absorption curves are of similar kind. In the case of horse serum, the minimum is at λ 2510 instead of λ 2540, and the curve for the protein band is of rather larger dimensions than the corresponding curve for human serum. The protein band of egg albumin is, on the other hand, more symmetrical in form, but the minimum absorption is at the same wave-length (λ 2540).

H. M. D.

The Chromophore Function. I. LIFSCHITZ (*Zeitsch. wiss. Photochem.*, 1916, **16**, 101—110).—A general statement of the author's views on the nature of chromophoric groups and their selective absorption effects. H. M. D.

Influence of Light on the Loss of Water of Crystallisation from Salts. ERNST BEUTEL (*Chem. Zentr.*, 1916, ii, 638; from *Osterr. Chem. Zeit.*, **19**, 123—124).—Well-defined crystals of chrome alum and cobalt magnesium sulphate were observed to lose water of crystallisation at those places where their surfaces were in contact with a metal support. These spots increase very rapidly in size when the crystals are exposed to light. The loss of weight in crystals exposed to ultra-violet and sun-light was respectively twice and two and a-half times that observed in crystals kept in the dark. H. W.

The Release of Radium Emanation from Water at Different Temperatures by the Bubbling Method. J. MORAN (*Trans. Roy. Soc. Canada*, 1916, [III], **10**, 57—66).—Experiments, in which a constant current of air was bubbled through a solution of radium at temperatures ranging from 16·5° to 80°, show that the emanation removed by the air increases with the temperature. When this method is employed in the estimation of the radium content, the solution should be kept at a constant and measured temperature. H. M. D.

Experimental Determination of the Ionisation Potential of Helium. CHARLES B. BAZZONI (*Phil. Mag.*, 1916, [vi], **32**, 566—575).—According to Bohr's theory, the energy required to remove one electron from a helium atom corresponds with 29·3 volts, whilst previous measurements of the ionisation potential have given 20 to 20·5 volts. In view of the agreement of Bohr's theory with experiment in so many directions, the ionisation potential of helium has been redetermined under conditions which avoid certain errors, which, it was thought, might be the cause of the discrepancy between theory and the earlier observations. The results obtained show that the true ionisation potential is not greater than 20 volts, and to reconcile the value with Bohr's theory it appears to be necessary to introduce new assumptions relative to the mechanism of the ionisation process. H. M. D.

Specific Smell Intensity and the Electrical Phenomenon of Cloud-like Condensed Water Vapours in Chemical Series. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 334—340).—Previous experiments have shown that the cloud of condensed water vapour, which is obtained by spraying aqueous solutions, has a positive charge when the dissolved substance is odorous. By comparing the quantities of the aliphatic alcohols and the fatty acids, which are required to arouse olfactory sensation, with the electrical effects produced when aqueous solutions of members of these two series of homologous substances are sprayed, it is found that the smell intensities correspond more or less with the power of the substances to give a positive charge to the water-droplets. It is supposed that both properties are connected with the lowering of the surface tension of water by the substances concerned. H. M. D.

Overvoltage Tables. IV. The Theories of Overvoltage and Passivity. EDGAR NEWBERY (T., 1916, **109**, 1359—1368).—Reviewing the results so far obtained by the author in his investigations of overvoltage (T., 1914, **105**, 2434; 1916, **109**, 1051, 1066, 1107), the conclusion is drawn that overvoltage is probably due to the high solution potentials of compounds of the electrode material with the discharged ion or with a product of the discharged ion. These compounds tend to form solid solutions in the electrode substance, and are usually stable only under the influence of high pressure or high temperatures. Passivity is due to the insolubility and good electrical conductivity of these compounds, which form a protective coating either over the whole metal surface or over the more easily soluble amorphous phase. This coating may consist of the pure compound or of a solid solution of the compound in the electrode substance.

The chemical stability of the higher oxides and hydrides is not to be measured by the overvoltage potentials; it is of more importance than the overvoltage when electrodes are used for the treatment of substances which are only oxidised or reduced slowly. Thus it is possible for an electrode that produces a comparatively stable hydride to effect reductions which another electrode of higher overvoltage is unable to do. For example, oleic acid is reduced at a copper, but not at a lead, electrode; also, nitrates are reduced to ammonia at a copper cathode, but to hydroxylamine at a lead cathode. T. S. P.

Occlusion of Hydrogen by a Palladium Cathode. DONALD P. SMITH and FREDERICK H. MARTIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2577—2594).—The electrical resistance and cathode potential in $2N$-sulphuric acid has been determined for palladium charged with hydrogen up to saturation. The measurements were made in the usual way, both while the wire was being charged electrolytically with hydrogen and after the charging current had been interrupted. It is shown that the proportional increase of resistance at apparent saturation varies widely even with wires made from the same sample of pure palladium. The resistance of saturated wires of 0·1 mm. diameter and less is shown to vary in a well-defined manner with the polarising current, and the resistance after the interruption of electrolysis is shown to undergo reversible and reproducible changes. In the case of wires of 0·32 mm. diameter, none of the above-mentioned changes are observed. It is shown to be probable that the changes of resistance of smaller wires are due to processes occurring within the metal and not far removed from its surface. It is tentatively suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state, in which it possesses an electrical conductance of its own, and passes gradually into another form which has either a much smaller conductivity or none at all. A number of characteristic changes have been observed after the interruption of electrolysis in the cathode potential of saturated palladium wire, and certain connexions have been noticed between the nature and

magnitude of these changes and the conditions of electrolysis. A few experiments have been carried out with copper wires which show that this metal does not change its resistance to a measurable extent when subjected to the same treatment as the palladium wires. A single experiment with nickel wire shows that it behaves in the same way as copper in this respect. J. F. S.

Free Energy and Heat Capacity. JAMES M. BELL (*J. Amer. Chem. Soc.*, 1916, **38**, 2629—2630. Compare *J. Physical Chem.*, 1905, **9**, 381).—Polemical. A criticism of Richards's use of some of Marignac's data on heat capacity (Marignac, *Ann. Chim. Phys.*, 1876, [v], **8**, 415). A note answering the criticism and justifying his position is appended by THEODORE W. RICHARDS to the paper (*ibid.*, 2631—2632). J. F. S.

The Stem Correction of Thermometers. EDWARD G. WHEELER (*J. Soc. Chem. Ind.*, 1916, **35**, 1198—1200).—During the course of a continuous distillation, it is frequently impossible, owing to lack of time, to make the necessary calculations for the correction of thermometric readings. To overcome this difficulty, the author has constructed a graph, which is fully reproduced in the original, from which the corrected temperature may be deduced after observations of the actual temperature recorded by the thermometer, the length of the external column, and the temperature of the latter, as determined by an attached thermometer. H. W.

Formula for the Calculation of the Specific Heat of Aqueous-alcoholic Solutions of Different Substances. N. A. KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 84).—The specific heats of aqueous-alcoholic solutions may be calculated by means of the empirical formula $C = 1 + n(C_0 - 1) + 0{\cdot}004x - 0{\cdot}00012x^2 + 0{\cdot}00000069x^3$, where C is the required specific heat of the aqueous-alcoholic solution of substance A, n the number of gram-equivalents of this substance per 200 mols. of water in the given aqueous-alcoholic solution, x the number of molecules of alcohol per 200 mols. of water, and C_0 the specific heat of an aqueous solution of 1 gram-equivalent of substance A in 200 gram-mols. of water. The value of C_0 is obtained from tables of physical constants. In thirty-four cases in which direct measurements were made of the specific heats of aqueous-alcoholic solutions, the difference between the experimental and calculated values was less than 0·005 in twenty-seven cases and between 0·006 and 0·010 in the remaining seven instances. T. H. P.

Free Energy of Dilution and the Freezing-point Lowerings in Solution of some Salts of Various Types of Ionisation, and of Salt Mixtures. RALPH E. HALL and WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1916, **38**, 2658—2676).—The lowering of the freezing point of aqueous solutions of mannitol, erythritol, sodium iodate, potassium iodate, potassium chloride, potassium nitrate, magnesium sulphate, potassium

sulphate, barium chloride, cobalt chloride, and lanthanum nitrate have been determined over a wide range of concentrations. Further measurements have been made of the freezing-point lowerings of equimolecular solutions of mixtures of sodium and potassium iodates, and potassium chloride and nitrate respectively. The temperature measurements were made by means of a fifty-pair thermocouple of copper constantan, and were accurate to 0·0001°. The values $\Delta t/N$ are plotted against the cube root of the concentration, and the degree of ionisation calculated in each case. In the case of mixtures, measurements were made over the range $0{\cdot}1N$—$0{\cdot}01N$ for each salt. The values of the degree of ionisation calculated from the results agree well with the mean of similar values of the individual salts. J. F. S.

Freezing-point Lowerings in Aqueous Solutions of Salts and Mixtures of Salts, and of a Salt with a Non-electrolyte. WILLIAM D. HARKINS and W. A. ROBERTS (*J. Amer. Chem. Soc.*, 1916, **38**, 2676—2679. Compare preceding abstract).—Using the method previously adopted, the freezing points of solutions of sodium sulphate, potassium sulphate, and their equimolecular mixture, sodium chloride, and a mixture of mannitol and potassium chloride, have been determined over a range of concentrations. The greatest temperature deviation from the calculated value was found in the case of the mixture of potassium chloride and mannitol, and this amounted to only 6/100000°. J. F. S.

An Improved Ebullioscope. A. SMITS (*Chem. Weekblad*, 1916, **13**, 1296).—A description of an improved form of the author's ebullioscope (*Chem. Weekblad*, 1904, **1**, 469), in which the tendency of the vapour generator to fracture is obviated. A. J. W.

Heat of Combustion of Wood Charcoal. N. I. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 54—75).—Various methods of drying charcoal to constant weight have been investigated. Satisfactory results are obtained by drying in a desiccator over sulphuric acid, and with charcoal which has been made for some time (a year or more), the dry weight obtained in this way is almost exactly the same as that given by five hours' heating in an oven at 103°, whilst a further heating for three hours is without appreciable influence. On the other hand, charcoal which has been recently prepared exhibits progressive increase in weight when heated at 103°, probably owing to oxidation, which also occurs, although slowly, at the ordinary temperature.

Eighteen samples of charcoal prepared from different kinds of wood, some in heaps and others in furnaces, have been analysed and investigated as to calorific value. The percentage of carbon varies from 73·04 to 92·11, and is always higher in heap charcoal than in retort charcoal; the proportion of hydrogen varies from 0·64% to 4·74%. The heats of combustion, calculated from the compositions by means of either Dulong's or Mendeléev's formula, are always less than the experimental values, and in general the divergence increases with the proportion of oxygen and nitrogen

taken together, although the introduction into these expressions of a correcting term is not possible.

Calculation from the author's experimental results shows that the number of calories generated by the combustion of 1 gram of charcoal is given by the expression $80{\cdot}51C + 273{\cdot}4H$, C and H representing the percentages of carbon and hydrogen in the dry charcoal. The errors of the values calculated by means of this formula lie between the limits $+0{\cdot}63\%$ and $-0{\cdot}47\%$, and for a sample of brown charcoal containing only 73·04% of carbon, and consisting of partly converted lignin, the error is only $+1{\cdot}48\%$.

T. H. P.

[Heat of Solution in Mixed Solvents.] N. A. KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 85—87).—The deductions drawn by Tanatar (A., 1915, ii, 742) from some of the results obtained by the author (A., 1913, ii, 22, 308, 671, 672) are erroneous.

T. H. P.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for Different Elements in Connexion with the Periodic System. III. Discussion of the Different Groups of Elements Separately. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 287—295. Compare A., 1916, ii, 386, 610).—If the total volume occupied by a liquid at the triple point is represented by v and the real volume of the molecules is b, then $(v-b)/v$ represents the ratio of the free volume to the total volume at the triple point. The evaluation of this ratio is discussed and the formula applied to hydrogen and the inert elements, for which $(v-b)/v$ is thus found to be approximately equal to 1/8.

H. M. D.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for Different Elements in Connexion with the Periodic System. IV. The Elements of the Halogen, Oxygen, and Nitrogen Groups. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 295—320. Compare preceding abstract).—The values of b_k and $\sqrt{a_k}$ have been calculated for the elements of the fifth, sixth, and seventh groups.

In a discussion of the values of the attraction constant, it is pointed out that the molecular condition of the element in the critical state has a very considerable influence on the value of $\sqrt{a_k}$. In a previous paper (A., 1916, ii, 610) it was suggested that the fact that the observed critical temperatures of certain elements are much higher than those calculated from $T_k = 78{\cdot}03a/b$ is due to the high degree of complexity of the molecules of these elements in the critical condition. Such complex molecules, in accordance with the additivity of $\sqrt{a_k}$, would show an abnormally large attraction constant. This view now appears to have been abandoned in favour of the hypothesis that monatomic molecules with free valencies exhibit abnormally large values of $\sqrt{a_k}$. The very high values of the attraction constant for antimony and bismuth are thus supposed to be due to the monatomic condition

of these elements in the critical condition. In regard to the other elements belonging to this group, arsenic consists of the mixture of 80% As_4 and 20% As molecules, phosphorus of molecules containing four atoms, and nitrogen of diatomic molecules.

The shadowing effect of univalent atoms on the central ter- or quadri-valent atoms with which the former are in combination is not always complete. If the hydrogen compounds of the elements of the nitrogen group are considered, it is found that the attraction of the central atom is completely eliminated in the case of nitrogen and phosphorus, but the attraction of the much larger arsenic and antimony atoms shows itself to some extent. In the case of arsenic, the diminished value of $\sqrt{a_k}$ is about one-third, and for antimony about one-half, the normal value.

The ratio of the free to the total volume at the triple point decreases from 1/8 for the elements of the helium to 1/20 for the elements of the nitrogen group. It is supposed that this ratio plays some part in determining the transition from the liquid to the solid state. H. M. D.

Thermodynamic Proof of Avogadro's Law. C. DEL LUNGO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 322—326).—Avogadro's law is the simplest and most natural hypothesis to explain Dalton's laws, but is usually deduced, independently of chemical laws, on the assumption that in gases having the same temperature the mean molecular energy is the same. From this proposition, first enunciated as a postulate by Clausius, and later shown to be a necessary consequence of Maxwell's law, may be derived also Gay-Lussac's law of the identity of the coefficient of expansion for all perfect gases. The postulate of Clausius, together with Avogadro's law as corollary, are thus confirmed by the experimental laws of Gay-Lussac and Dalton, but since the inverse demonstration cannot be made, it cannot be asserted with absolute safety that the postulate is necessary and true; it remains a sufficient and highly probable hypothesis, its probability being increased by various considerations which were advanced by Clausius, and are based on the fact that, when two gases at the same temperature are mixed, the mixture also has this temperature.

The author gives a proof of Gibbs's theorem on the entropy of gaseous mixtures, namely, the entropy of a mixture of gases is the sum of the entropies of the component gases when each occupies the total volume at the same temperature. Assumption of the invalidity of the Clausius postulate then leads to the inadmissible conclusion that a diminution of entropy may occur in a reversible process. This postulate, on which Avogadro's and Gay-Lussac's laws directly depend, is therefore rigorously and simply demonstrated. T. H. P.

A New Method for the Determination of Vapour Densities. X. PHILIP BLACKMAN (*Chem. News*, 1916, **114**, 307).—The bulb in which vaporisation takes place consists of an inverted flask, the neck of which passes through an aperture in the base of a thermostat. H. M. D.

The Application of Vortex Rings in the Determination of Surface Tensions. VIKTOR KUTTER (*Physikal. Zeitsch.*, 1916, **17**, 573—579). The method described depends on the measurement of the period of vibration of drops of the liquid when falling under the action of gravity, and its novelty consists in the device which is adopted for the determination of the time of vibration. The drops are allowed to fall into a second liquid of somewhat greater density, producing vortex rings which penetrate to a depth which depends on the phase of the vibrating drop at the moment when it penetrates the surface of the indicating liquid. By increasing the difference between the level of the tip of the tube at which the drops are formed and the surface of the indicating liquid, this phase may be altered in a continuous manner, and the actual observations consist in determining the difference in the fall which corresponds with a half-period in the vibrating drop. From this difference in the fall, the period of vibration can be easily calculated.

To make the vortex rings clearly visible, the indicator liquid must be suitably chosen, and the particular method described makes use of a solution of some substance which reacts with the dropping liquid or with substances dissolved in this, with the formation of an insoluble substance, which, however, dissolves in excess of the indicator solution. An acidified solution of antimony chloride may thus be used as an indicator for aqueous solutions of many different substances, the vortex ring being rendered visible as the result of the precipitation of antimony oxychloride.

The formation of a precipitate is not necessary, as a matter of fact, and in the case of drops of a solution of potassium permanganate, the vortex rings can be studied with the aid of a solution containing ferrous sulphate and sulphuric acid. In general, the formation of a precipitate affords the most suitable method for observing the vortex rings, and a large number of pairs of solutions, which can be used in combination, are tabulated in the paper. H. M. D.

The Temperature-coefficient of the Free Molecular Surface Energy of Liquids between $-80°$ and 1650°. XV. The Determination of the Specific Gravity of Molten Salts and of the Temperature-coefficient of their Molecular Surface Energy. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 381—397. Compare A., 1916, ii, 126, 128).—The data obtained in measurements of the molecular surface energy of molten salts at various temperatures are recorded. The temperature-coefficients derived from these are given in the following summary, together with the formulæ from which the density (D_4^t) may be calculated. Lithium fluoride, 0·40—0·58, $D=1·798-0·0004375(t-850)$; lithium chloride, 0·47, $D=1·501-0·000432(t-600)$; lithium sulphate, 0·50, $D=2·008-0·000407(t-850)$; lithium nitrate, 0·45, $D=1·755-0·000546(t-300)$; sodium fluoride, 0·52, $D=1·942-0·000564(t-1000)$; sodium chloride, 0·48, $D=1·549-0·000626(t-800)$; sodium bromide, 0·53,

$D = 2{\cdot}306 - 0{\cdot}00072(t-780) - 0{\cdot}0^68(t-780)^2$; sodium iodide, 0·29—0·63, $D = 2{\cdot}698 - 0{\cdot}001061(t-700)$; sodium sulphate, 0·30, $D = 2{\cdot}061 - 0{\cdot}000483(t-900)$; sodium molybdate, 1·2—0·56, $D = 2{\cdot}795 - 0{\cdot}000629(t-700)$; sodium tungstate, 0·64—0·98, $D = 3{\cdot}673 - 0{\cdot}0009275(t-930) + 0{\cdot}0^6337(t-930)^2$; sodium nitrate, 0·24—0·45, $D = 1{\cdot}914 - 0{\cdot}000672(t-300)$; sodium metaphosphate, 0·43—1·1, $D = 2{\cdot}193 - 0{\cdot}00044(t-800)$; potassium fluoride, 0·33—0·83, $D = 1{\cdot}878 - 0{\cdot}000669(t-900)$; potassium chloride, 0·68, $D = 1{\cdot}539 - 0{\cdot}0005947(t-750)$; potassium bromide, 0·76, $D = 2{\cdot}106 - 0{\cdot}000799(t-750)$; potassium iodide, 1·58—0·41, $D = 2{\cdot}431 - 0{\cdot}001022(t-700)$; potassium sulphate, 0·90, $D = 1{\cdot}872 - 0{\cdot}000545(t-1100)$; potassium dichromate, 0·86, $D = 2{\cdot}285 - 0{\cdot}000695(t-400)$; potassium molybdate, 0·79, $D = 2{\cdot}342 - 0{\cdot}00060(t-964) - 0{\cdot}0^6128(t-964)^2$; potassium tungstate, 1·6, $D = 3{\cdot}113 - 0{\cdot}00082(t - 1000) + 0{\cdot}0^6162(t - 1000)^2$; potassium nitrate, 0·83, $D = 1{\cdot}898 - 0{\cdot}0007681(t-300)$; potassium metaphosphate, 0·91—1·28, $D = 2{\cdot}111 - 0{\cdot}00043(t-800)$; rubidium fluoride, 1·0—0·40, $D = 2{\cdot}873 - 0{\cdot}000967(t-825) - 0{\cdot}0^6247(t-825)^2$; rubidium chloride, 1·02, $D = 2{\cdot}129 - 0{\cdot}000823(t-700)$; rubidium bromide, 0·77, $D = 2{\cdot}688 - 0{\cdot}001096(t-700)$; rubidium iodide, 0·95, $D = 2{\cdot}798 - 0{\cdot}001107(t-700)$; rubidium sulphate, 1·98—0·27, $D = 2{\cdot}562 - 0{\cdot}000665(t-1050)$; rubidium nitrate, 0·78, $D = 2{\cdot}492 - 0{\cdot}000972(t-300)$; cæsium fluoride, 0·72—0·36, $D = 3{\cdot}611 - 0{\cdot}001234(t-700)$; cæsium chloride, 0·80—1·70, $D = 2{\cdot}786 - 0{\cdot}00108(t-650)$; cæsium bromide, 0·90—0·57, $D = 3{\cdot}125 - 0{\cdot}00134(t-650)$; cæsium iodide, 0·82, $D = 3{\cdot}175 - 0{\cdot}001222(t-640)$; cæsium sulphate, 1·91—0·43, $D = 3{\cdot}034 - 0{\cdot}000711(t-1040) - 0{\cdot}0^6494(t-1040)^2$; cæsium nitrate, 1·18—0·42, $D = 2{\cdot}824 - 0{\cdot}001114(t-400)$; thallous nitrate, 0·81, $D = 4{\cdot}917 - 0{\cdot}00175((t-200)$; stannous chloride, 1·0, $D = 3{\cdot}298 - 0{\cdot}001253(t-300)$. In the determination of the densities, a hydrostatic method was employed.

By comparison with organic liquids, for which the normal value of the temperature-coefficient is about 2·24, the above data show that the temperature-coefficient for molten salts is much smaller. Although no general regularity is evident, it seems that for corresponding haloid salts of the alkali metals, the temperature-coefficient has a tendency to increase with the atomic weight of the metal. The low value of the temperature-coefficient of the molecular surface energy of molten salts has frequently been supposed to indicate a high degree of association, but the authors doubt the validity of this conclusion on the ground that such ionised salts do not conform to the requirements of the theory of corresponding states, and that the degree of ionisation varies considerably with the temperature. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids between − 80° and 1650°. XVI. The Surface Tension of some Halogen Compounds of Sulphur, Phosphorus, Arsenic, Antimony, and Bismuth. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 397—404. Compare previous abstract).—The temperature-coefficients of the molecular surface energy and the

formulæ expressing the variation of the density with the temperature are given in the following summary: sulphur monochloride, 2·24—1·79, D 1·7094 at 0° and 1·492 at 138°; phosphorus trichloride, 1·61, D 1·582 at 16·4° and 1·527 at 46·2°; phosphorus tribromide, 0·81—2·63; arsenic trichloride, 1·40, $D = 2·2050 - 0·001856t - 0·0^5 27t^2$; arsenic tribromide, 2·05—0·98, $D = 3·3972 - 0·002822(t-25) + 0·0^5 248(t-25)^2$; antimony trichloride, 1·66; bismuth trichloride, 2·14—1·78, $D = 3·860 - 0·00232(t-250)$; bismuth tribromide, 1·76—2·0, $D = 4·598 - 0·0026(t-250)$.

Although the temperature-coefficient is generally less than the normal value, it is in all cases much greater than the average value obtained for molten inorganic salts. The difference is to be ascribed to the smaller contrast in the electrochemical character of the components and the absence of ionisation.

When the surface tensions of the chlorides or the bromides at the same temperature are compared, it is found that the surface tension increases with the atomic weight of the positive element. This is the reverse of what was previously found in comparing the haloids of the alkali metals.

For the same positive element, the surface tension increases with the atomic weight of the halogen, which is again the reverse of the behaviour shown by the alkali metal haloids. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids between −80° and 1650°. XVII. The Relations between the Molecular Cohesion of Liquids at their Melting- and Boiling-points and their Absolute Melting- and Boiling-temperatures Respectively. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 405—414).—According to Walden (compare A., 1909, ii, 122), the value of Ma^2/T for non-associated substances is equal to 1·156 at the boiling point and 3·65 at the melting point. The material accumulated by the author has been applied in the further investigation of these empirical formulæ. The substances concerned are divided into four groups, the first of which contains 121 compounds, and includes all the substances for which the relation holds approximately so far as the boiling point is concerned. The mean value of $K_b = Ma^2_b/T_b$ is 1·12 and of $K_m = Ma^2_m/T_m$ is 3·38. The mean value of the constant at the melting point is thus three times that at the boiling point.

The second group contains sixteen organic compounds, for which K_b has an appreciably smaller value, and the third group fourteen compounds, for which K_b is either much greater than 1·12, or, as in the case of certain glycerides, for which K_m is very large in comparison with the normal value. The fourth group includes forty-eight inorganic compounds and metallic salts, and the abnormally small values of K_m for the latter show that the empirical relation does not apply at all to molten salts. The halogen compounds of the elements of the nitrogen group approximate much more closely to the requirements of the empirical formulæ. H. M. D.

New Classification of the Processes of Adsorption and Importance of the Theory of Adsorption for Various Branches of Natural Science; Adsorption of Solutions by Porous Substances. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 90—94).—From the cases of adsorption which have been previously studied, principally by the author and his collaborators, the following classification of different types of adsorption is deduced.

I. Reversible adsorption: (*A*) Partial adsorption: (*a*) adsorption without separation, most of the adsorptions as yet known being of this type; (*b*) separative or fractionating adsorption, as yet unknown. (*B*) Exhaustive adsorption: (*a*) adsorption without separation, possible examples of this existing; (*b*) separative or fractionating adsorption, the adsorption of the solid paraffins of petroleum by floridin (A., 1915, i, 489) being of this type.

II. Irreversible adsorption: (*A*) Partial adsorption: (*a*) adsorption without separation, examples of which are (1) dyeing with fast dyes, and (2) adsorption of casein from solutions in borax solution by means of aluminium hydroxide; (*b*) separative or fractionating adsorption, as yet unknown. (*B*) Exhaustive adsorption: (*a*) adsorption without separation, examples of this being (1) adsorption of pepsin from aqueous solution by means of aluminium hydroxide, (2) adsorption of α-gelatin, and (3) of β-gelatin by the same adsorbent; (*b*) separative or fractionating adsorption, examples of which are (1) adsorption of egg-albumin from aqueous solution by aluminium hydroxide, (2) adsorption of the peptone of egg-albumin from aqueous solution by the same adsorbent, (3) probably the adsorption of toxins from different serums, the anti-toxins remaining in solution (compare Zunz, *Zeitsch. Immunitätsf.*, 1913, **19**, 326), and (4) adsorption of iodide of starch by aluminium hydroxide.

In a discussion on the practical aspects of adsorptive processes, attention is directed (1) to the removal of the solid paraffins from petroleum, which is thus more easily transported through pipes during the winter, and (2) to the successful application of *Bolus alba* to the treatment of cholera on the Serbian front during the Balkan War of 1913. T. H. P.

Behaviour of Ferric Oxide and Hydroxide towards Aqueous Solutions of Hen's Egg-albumin. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 95).—Whereas dry aluminium hydroxide is an excellent adsorbent, and the adsorptive capacity of dry alumina is only three to four times less than that of the hydroxide, neither ferric hydroxide nor oxide exerts any adsorptive action when immersed for twenty-four hours in an aqueous solution of hen's egg-albumin. Since the albumins are adsorbed more readily than other substances, it may be concluded that the latter will not be adsorbed by ferric hydroxide or oxide. T. H. P.

Aluminium Oxide and Hydroxide as Adsorbents and their Behaviour towards Aqueous Solutions of Hen's Egg-albumin. M. A. RAKUZIN and (MLLE.) EK. MAKS. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 95—97. Compare A., 1915, i, 1015; 1916, i, 90).—Only when chemically pure does aluminium hydroxide exert its full adsorptive power on aqueous solutions of the albumin of hen's eggs. Commercial precipitated alumina is applicable as an adsorbent only when dried to constant weight in a steam oven, such aluminium hydroxide then giving identical results in the hands of different investigators. The adsorptive power is diminished by the presence of moisture. Aluminium oxide exerts only a feeble adsorptive action on albumin solutions. The above conclusions appear to hold also for solutions of other substances than albumin. T. H. P.

Limiting Concentrations in the Adsorption of Aqueous Solutions of Hen's Egg-albumin by Aluminium Hydroxide; Stoicheiometry of Processes of Adsorption. M. A. RAKUZIN, G. D. FLIER, and M. A. BLOCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 99—105. Compare A., 1915, i, 1015).—The authors have studied the adsorption at the ordinary temperature of hen's egg-albumin from aqueous solutions of different concentrations by means of aluminium hydroxide, the amount of the latter used being in each case 10% of the weight of the solution. The results obtained show that, when the concentration of the albumin in the solution is equal to or greater than 9%, no adsorption by aluminium hydroxide takes place. The curve connecting the proportion of total albumin adsorbed with the initial concentration of the solution is approximately logarithmic, marked divergence occurring only as the curve approaches the concentration axis. The marked diminution of the adsorption in the latter region is probably related to the increased internal friction of the solution, which renders difficult the penetration of the molecules of the adsorbed substance into the ultramicroscopic capillaries of the adsorbing particles.

Quantitative and exhaustive adsorption occurs only when the quantity of adsorbent is sufficient and its quality suitable; further increase in the quantity is then useless. Between the quantities of adsorbent and adsorbed substance (albumin, paraffin, etc.), the existence of a stoicheiometrical relation is therefore assumed. Such relation is regarded as based on the concentration equation of Ostwald and Freundlich, the quantity of substance adsorbed being inversely proportional to the initial concentration. The results are considered in relation to Freundlich's formula, $x/m = \beta c_1^{1/p}$, where m is the quantity of adsorbent, c_1 the equilibrium concentration, and β and $1/p$ constants depending on the temperature and on the nature of the substance; the values of these constants in the present case are found to be 0·075 and 0·178 respectively. For concentrations of the albumin up to about 6%, the calculated and experimental values of x/m are in satisfactory

agreement, but for higher concentrations the deviations are very considerable. T. H. P.

The Dissociation Equilibrium of Nitrosyl Chloride, $2NO + Cl_2 \rightleftarrows 2NOCl$. II. Replacement of the Chemical Constants by Integration Constants calculated from the Molecular Dimensions. MAX TRAUTZ and CLAUS FRIEDRICH HINCK (*Zeitsch. anorg. Chem.*, 1916, **97**, 127—138. Compare A., 1916, ii, 304, and following abstract).—The formerly accepted figures for the heat change in this dissociation are criticised, and it is shown that the value should be about 18,000 cal. instead of 28,800, the integration constant becoming zero instead of 4·9. Values almost identical with these are obtained from the authors' measurements. The equation for the equilibrium then becomes $\log K = -3680/T + 1{\cdot}5 \log T$. The diameter of the intermediate molecule, probably $NOCl_3$, is calculated to be $11{\cdot}6 \times 10^{-8}$ cm. C. H. D.

The Dissociation Equilibrium of Nitrosyl Chloride, $2NO + Cl_2 \rightleftarrows 2NOCl$. MAZ TRAUTZ and LILI WACHENHEIM (*Zeitsch. anorg. Chem.*, 1916, **97**, 241—284. Compare preceding abstract). —The former determinations of Trautz and Hinck gave good agreement with theory for the range of temperature 560—590° abs., but not below that range. Using the same apparatus as before, the velocity of dissociation at $T = 273$ and 434 has been determined. The equilibrium has also been determined at temperatures below $T = 500$, using the same apparatus. The measurements show that complete union to form NOCl takes place, but that there is a small further contraction, possibly due to formation of $(NO)_2Cl$. A new apparatus has been designed to admit successive small quantities of chlorine to nitric oxide, and similar experiments have been made in that manner. The heat of formation at $T = 290$ has also been determined calorimetrically, the value $Q_0 = 16{,}841$ cal. being obtained. The conclusions of the investigation are stated in the preceding paper. C. H. D.

The Dissociation of Phosphorus, and the Detonating Gas Cell in the Light of the New Theory of Gas Reactions and a New Interpretation of the Approximate Additivity of $C_v - \frac{3}{2}R$ for Gases. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1916, **97**, 113—126. Compare *ibid.*, 1916, **96**, 1; Stock, Gibson, and Stamm, A., 1913, ii, 43).—The diameter of the P_4 molecule has been recalculated, using Stock's data, and the more probable value of 20×10^{-8} cm. has been obtained.

The usual data for the dissociation of steam lead to improbable values. Reasons are given for doubting the generally accepted values for the degree of dissociation and for the *E.M.F.* of the detonating gas cell, higher values of both being probable.

In applying the principle of additivity, the assumption is generally made that each gas consists of only one kind of molecules. If, however, several 'thermal isomerides' are present, the heat of

isomerisation must be taken into account, and a small correcting term must be introduced. This correction is in most cases so small that satisfactory results are obtained without applying it.

C. H. D.

Diffusion in Liquids. BASIL W. CLACK (*Proc. Physical Soc., London*, 1916, **29**, 49—57).—The results obtained in previous experiments (A., 1909, ii, 125; 1915, ii, 45) on the diffusion of sodium chloride, potassium chloride, and potassium nitrate in aqueous solution have been recalculated by the introduction of a correction suggested by Griffiths.

A new method is also described of calculating the coefficient of diffusion at any specified concentration from the experimental data. It is said that this gives more certain results than those obtained by the methods previously employed.

H. M. D.

Influence of Pressure on Solubility. HERBERT F. SILL (*J. Amer. Chem. Soc.*, 1916, **38**, 2632—2643).—By means of a pressure apparatus, which allows of samples being removed without lowering the pressure, the author has determined the solubility of sodium chloride and barium hydroxide in water at 25° under various pressures. A full description of the pressure apparatus is given. The following solubility values are given for sodium chloride at 25° per 100 grams of solution, 26·44 at 1 kilo. pressure, 26·58 at 250 kilos., 26·72 at 500 kilos., and 26·82 at 750 kilos. pressure. In the case of barium hydroxide, the values are 8·304 at 1 megobar, 8·779 at 245 megobars, and 9·366 at 490 megobars pressure. The heat of solution at the saturation point is extrapolated to 51·2 cal. for the octahydrate of barium hydroxide. This value is got from the experimentally found heat changes observed in bringing a 54% saturated solution to 64% and a 64% solution to 74% respectively. Both values were obtained by using the Richards adiabatic calorimeter. The specific volume change per gram of dissolved substance was experimentally determined by a dilatometric method, and found to be 0·0508. Finally, the temperature-coefficient of the solubility was calculated to 0·288%. The whole of the data for evaluation of the equation

$$T(p_2-p_1)(v_2-v_1)/(t_2-t_1)=Q$$

is thus obtained for barium hydroxide. It is shown that the left-hand side of the equation has the value $2·16\times10^9$, whilst the right-hand side has the value $2·14\times10^9$.

J. F. S.

Effect of Salts on the Solubility of Other Salts. VIII*a*. The Solubility Relations of a Very Soluble Bi-univalent Salt. WILLIAM D. HARKINS and HARRY M. PAINE (*J. Amer. Chem. Soc.*, 1916, **38**, 2709—2714. Compare A., 1912, ii, 28).—The solubility of strontium chloride in water and in solutions of strontium nitrate, sodium nitrate, nitric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, potassium iodide, potassium chloride, cupric chloride, and potassium nitrate of various concentrations have been determined at 25°. The densities of all solu-

tions have also been recorded. Strontium chloride dissolves in water to the extent of 557·6 grams in 1000 grams of water, and the solution has a density D_4^{25} 1·4015. Strontium nitrate increases the solubility to 558·5 grams with 0·1372 equivalent, and then decreases it to 551·4 grams with 3·318 equivs. per 1000 grams of water. Sodium nitrate increases the solubility to 584·8 grams with 3·553 equivs., and then decreases it to 542·6 grams with 6·856 equivs. per litre. Nitric acid has very little influence on the solubility, whereas hydrochloric acid strongly depresses the solubility to 42·09 grams with 9·205 equivs. per 1000 grams. The other substances examined all depress the solubility of strontium chloride appreciably, but not to anything like the extent that hydrochloric acid does. The solubility curve for hydrobromic acid lies above that for hydriodic acid, and hydrochloric acid, on account of its common ion effect, gives a curve which lies much below either. Just as hydrochloric acid depresses the solubility more than hydrobromic acid, so potassium chloride is more effective in lowering the solubility than potassium iodide. The curves for sodium nitrate and nitric acid have the same relative positions as potassium iodide and hydriodic acid and potassium chloride and hydrochloric acid. In all these cases, the solubility of strontium chloride is less in the acid than in the corresponding salt solution.

J. F. S.

Effect of Salts on the Solubility of Other Salts. VIII*b*. Solubility Relations of some Extremely Soluble Salts. WILLIAM D. HARKINS and W. TUDOR PEARCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2714—2717. Compare preceding abstract).—The solubility of strontium bromide in solutions of strontium nitrate, and of potassium ferrocyanide in sodium ferrocyanide solutions, and sodium ferrocyanide in potassium ferrocyanide solutions of various concentrations, have been determined at 25°. Strontium bromide dissolves in water to the extent of 1066·1 grams per 1000 grams of water at 25°, and the solution has a density D_4^{25} =1·7002. The following values have been obtained for the solubility of strontium chloride in grams per 1000 grams of water in solutions of the following molecular concentrations of strontium nitrate, and the solutions have the appended densities:

Solubility $SrBr_2$...	1066·2	1066·95	1067·42	1068·54	1068·9	1069·17	1073·97
Conc. $Sr(NO_3)_2$ ...	0·0000	0·0360	0·07216	0·14568	0·3066	0·61124	1·8610
D_4^{25}	1·7002	—	1·70325	1·72844	1·73766	1·74866	1·77368

Potassium ferrocyanide dissolves in water at 25° to the extent of 247·96 grams per 1000 grams of water, and the solution has a density D_4^{25} =1·09081. The solubility decreases in sodium ferrocyanide solution until the concentration of the latter reaches 0·12306 mol., after which it continuously increases. Sodium ferrocyanide dissolves in water at 25° to the extent of 207·25 grams per 21000 grams of water, and the solution has a density D_4^{25} =1·0595. The solubility continuously increases in potassium ferrocyanide solution with increasing concentration up to 291·40

grams per 1000 grams of water with 1·0578 mols. of potassium ferrocyanide. J. F. S.

Ionisation and Solubility Relations of Salts of Higher Types. IV. Intermediate Ions in Solutions of Uni-bivalent Salts, and of Lanthanum Iodate, a Ter-univalent Salt. WILLIAM D. HARKINS and W. TUDOR PEARCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2679—2709. Compare A., 1912, ii, 27, 28, and preceding abstracts).—A theoretical discussion is entered into on the influence of salts of various types on the solubility of a salt of multi-ion type, both on the basis that intermediate ions exist and also that they do not exist. To examine the case experimentally, the solubility of lanthanum iodate, alone and in the presence of lanthanum nitrate, potassium iodate, sodium iodate, sodium nitrate, and lanthanum ammonium nitrate of various concentrations has been determined at 25°. The electrical conductivity and the density of the solutions have also been determined at the same temperature. It is shown that at 25° lanthanum iodate dissolves to the extent of 0·6841 gram per litre, and the solution has a density D_4^{25} 0·998251. In the presence of lanthanum nitrate, the solubility falls continuously with increasing concentration of lanthanum nitrate to a minimum, which is 0·5194 gram per litre with 10·0 millimols. of nitrate, after which it rises to 0·7431 with 200·52 millimols, of the nitrate. In the case of potassium iodate, the solubility falls continuously and reaches the value 0·37388 gram per litre with 1·9828 millimols. Sodium iodate depresses the solubility even more, the value 0·0973 gram per litre being obtained with 6·7989 millimols per litre. Sodium nitrate increases the solubility to 3·030 grams per litre with 3200 millimols. Lanthanum ammonium nitrate also effects a large increase in the solubility. A series of electrical conductivity determinations of all the solutions investigated has also been made. Calculations of the constituents of the mixtures of the solutions were made, and curves drawn to show the changes in the solubility products and concentrations of the non-ionised part with changes in the total ion concentration. In these calculations, intermediate ions are assumed to be non-existent. It was found that the apparent concentration of the non-ionised part is affected normally by the addition of non-common ion salts; it is affected abnormally by the presence of salts having a common univalent ion in that it gives an extraordinary depression, and it is affected even more abnormally by the addition of salts having a common tervalent ion, giving a rapid rise in the apparent solubility. These abnormalities disappear if intermediate ions are assumed to be present. J. F. S.

Neutral Salt Action on Acid Solubilities. WILLIAM ROLAND HENDERSON and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1916, **20**, 663—679).—The solubility of calcium oxalate in 0·5*N*-solutions of hydrochloric, trichloroacetic, and chloroacetic acids in presence of varying quantities of the corresponding potassium salts has been

measured at 25°. Similar measurements were made with calcium tartrate and 0·5N-solutions of chloroacetic and acetic acids.

The results show that the salt effect varies according to the strength of the acid, and in general increases with the concentration of the salt. The salt produces an increase in the solubility in the case of hydrochloric acid, a slight decrease when trichloroacetic acid is used as solvent, and a very marked decrease in the case of chloroacetic acid. The reduction of the solvent action is still greater when acetic acid is used, but the salt effect in this case appears to reach a maximum at about 0·1N-salt concentration.

The addition of potassium nitrate to hydrochloric acid has very nearly the same effect as the addition of potassium chloride, and a very large positive effect is obtained when potassium chloride is added to the acetic acid solution.

The observed salt effects are compared with those which have been found in the investigation of acid catalysis. The comparison shows that there is some correspondence between the two effects, but that this is by no means complete. H. M. D.

The Interpretation of the Röntgenograms and Röntgen Spectra of Crystals. A. SMITS and F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 432—438).—The authors criticise the crystal models which have been devised for various substances on the basis of X-ray spectroscopic observations. It is pointed out that this method of analysis only gives the distances between the centres of the constituent atoms, and affords no information relative to the actual spaces between the atoms. It is very probable that the distances between the molecules are smaller than the molecular diameter, and it follows that the distance between atoms which belong to different molecules will not be much greater than the distance between atoms in the same molecule. In spite of this approximate equality, the authors contend that the crystal models ought to differentiate between those atoms which are chemically combined in the same molecule and those which are constituents of different molecules. The view that chemical attraction is localised in centres, the number of which is determined by the valency of the atom, is not easily reconciled with configurations which make no distinction between atoms of the same and atoms of different molecules.

A model representing the structure of sodium chloride has been devised in which the valency relations characteristic of the chemical compound are taken into account. This differs from the model put forward by Bragg, but it is claimed that it is equally in agreement with the X-ray data. For the details of the space-lattice arrangement the original must be consulted. H. M. D.

Crystals as Molecular Compounds. II. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1916, **97**, 161—174. Compare A., 1916, ii, 228).—The diamond is, so far, the only crystal the structure of which as revealed by the X-rays accords exactly with the valency of the atom. In this case, the valency and co-ordination numbers

are the same. Zinc blende has a very similar structure, but each zinc atom is now symmetrically surrounded by four sulphur atoms, and each sulphur atom by four zinc atoms, as represented by the symbol $[ZnS_4]$ or $[SZn_4]$. The radicle, (RS_4), actually occurs in many thio-salts. That both positive and negative radicles may occur in molecular compounds is shown by the existence of such compounds as $[NR_4][AuCl_4]$. Zinc blende may therefore be regarded as a polymolecular double sulphide, built up according to the rules of co-ordination. In sodium chloride, the co-ordination number is six, and the atoms are placed at alternate cube angles. In accordance with this, all molecular compounds in which the central atom has the co-ordination number six exhibit octahedral grouping.

Fluorite closely resembles blende. Each fluorine atom is symmetrically placed in regard to four calcium atoms, and each calcium atom in regard to eight fluorine atoms. The co-ordination number four corresponds with the general properties of fluorine, whilst the number eight for calcium agrees with the formulæ of such compounds as $[Ca(NH_3)_8]Cl_2$.

Copper and silver have a face-centred cubic lattice, so that each atom stands in similar relation to twelve other atoms, indicating the co-ordination number twelve. Intermetallic compounds may be regarded as molecular compounds, and it is noteworthy that the amalgams contain compounds KHg_{12}, $RbHg_{12}$, $SrHg_{12}$, and $BaHg_{12}$, the number 12 being independent of the valency.

The co-ordination centres may be groups of atoms instead of single atoms. The crystalline structure of anhydrite may be derived from that of sodium chloride by replacing the elementary cube by the rhomb, and then substituting calcium atoms for sodium and SO_4 groups for chlorine. The complex radicles are then $[Ca(SO_4)_6]$ and $[(SO_4)Ca_6]$, the group SO_4 taking the place of a single atom. This replacement of a halogen atom by a bivalent negative group is known in the complex cobalt and platinum salts, such as $[Co(NH_3)_5Cl]X_2$ and $[Co(NH_3)_5(SO_4)]X$. The grouping about atomic radicles as co-ordination centres in place of single atoms may be expected to give less symmetrical structures than in the case of central atoms, and this accords with the fact that anhydrite is not regular, but rhombic. The co-ordination valencies of the SO_4 group are therefore not of equal value. In pyrites, the symmetry is like that of sodium chloride, the groups being $[Fe(S_2)_6]$ and $[(S_2)Fe_6]$. Pyrite is thus to be regarded as a persulphide.

The co-ordination number of both the calcium and the CO_3 radicle in calcite is six. C. H. D.

Mixed Crystals, $(Mg,Zn)SO_4,7H_2O$. C. VIOLA (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 285—299. Compare this vol., ii, 80).—A crystallographic study has been made of heptahydrated zinc and magnesium sulphates, and of their mixed crystals. From the manner in which these crystals undergo alteration in a dry atmosphere, and from the appearance of certain vicinal faces in

the mixed crystals and not in the crystals of the pure components, the conclusion is drawn that the mixed crystals, $(Mg,Zn)SO_4 + 7H_2O$, are constituted of alternate very thin layers of $MgSO_4 + 7H_2O$ and $ZnSO_4 + 7H_2O$, yielding a homogeneous and continuous complex. Mixed crystals are therefore homogeneous mechanical mixtures, and not physical mixtures like van't Hoff's solid solutions. Such a conclusion is not contradicted by considerations based either on the total and free energy or on the modern views of crystal structure. T. H. P.

Emulsions and Suspensions with Molten Metals. H. W. GILLETT (*J. Physical Chem.*, 1916, **20**, 729—733).—Attention is directed to problems of colloidal chemistry in connexion with molten metals and alloys, and to the importance of these in the metal industries. H. M. D.

Gibbs's Phase Rule. CARLO VIOLA (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 245—251).—The author discusses the various definitions which have been suggested for phases, and points out that the essential character on which complete agreement exists is that of homogeneity, a break in this indicating passage from one phase to another. As regards homogeneity, however, doubt may occur, since the boundary between homogeneity and heterogeneity must be determined experimentally, and, consequently, depends on the methods of observation available.

Since, therefore, homogeneity is an arbitrary and indefinable character, and use cannot be made of the idea of mechanical separability in the definition of phases, the only remaining character is the principle of energy. If, then, a homogeneous complex is dissolvable with consumption of work, and can resume its original condition with evolution of work, it assumes the character of a phase. Thus a solution (solid or liquid) is a phase, since the solute cannot be separated from the solvent without expenditure of work, and cannot again enter into solution without yielding the same amount of work. The same may be said of homogeneous mechanical mixtures when the very fine heterogeneous particles composing them are not separable without a sufficient expenditure of work. In order to separate two very fine particles in intimate contact, the surface and the surface tension, and hence also the energy, are increased. For this reason a conglomerate or a dissolved mechanical mixture, the heterogeneous components of which have the whole of their contour in contact with the solvent, is not a phase. The properties of the triclinic felspars are in accord with those of either a solid solution or a homogeneous mechanical mixture, and these minerals are to be regarded as phases.

The fundamental conditions on which the phase rule is based are examined, and it is shown that this rule is applicable to the equilibrium of homogeneous mechanical mixtures considered as phases in contact with other phases, provided that they are

reversible in any transformation occurring within the existence of the system.

The case of mixed crystals of heptahydrated zinc and magnesium sulphates is considered later (this vol., ii, 79). T. H. P.

The Equilibrium Solid–Liquid–Gas in Binary Systems which present Mixed Crystals. III. H. R. KRUYT and W. D. HELDERMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 439—447. Compare A., 1910, ii, 195, 837).—The conditions regulating the co-existence of solid, liquid, and gas phases in the system iodine–bromine have been determined by tensimetric observations on various mixtures. The pressure–temperature curve shows a maximum at 23° and a sharp minimum at 44°, whilst the existence of a further maximum at about 100° is indicated. In this system, the compound IBr is formed, and this compound is probably miscible in all proportions with both the components. The pressure–temperature curve with two maxima and an intermediate minimum is supposed to be characteristic of systems in which the components form a series of mixed crystals and a compound which is also miscible with the components. H. M. D.

Equilibrium of the Binary Mixture, Phenol–Aniline, near the Distectic Point. V. VOANO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 76—84).—Lidbury (A., 1902, ii, 242) found that the maximum melting point for this system is shown by the mixture containing 49 mols. % of aniline, and not 50 mols. % of aniline, which would correspond with the pure aniline phenolate. The author finds, on repeated determination of the solidifying point of one and the same mixture, that this temperature sometimes remains constant within the limits of experimental accuracy and sometimes undergoes a distinct change. Thus the mixture containing 49·95 mols. % of aniline gave successively the solidifying points 30·580°, 30·578°, 30·580°, and 30·520°. It is found, further, that in the neighbourhood of the distectic point there are two distinct curves for this system, the maxima corresponding (1) with 50 mols. % of aniline, and (2) with 49·1 mols. % of aniline. The causes of this result are regarded as (1) the slow decomposition of the aniline phenolate on fusion, and (2) the tendency of the phenolate, deposited from the solutions with excess of phenol, to form solid solutions. T. H. P.

Rate of Hydrolysis of Potassium Cyanide in Aqueous Solution. JAN ZAWIDZKI and TADEUSZ MIECZYNSKI (*Chem. Zentr.*, 1916, ii, 730; from *Kosmos* (Lemberg), 1914, **38**, 1366—1375).—The authors have studied the kinetics of the auto-hydrolysis of potassium cyanide in aqueous solution at 100°, 110°, and 120°, and are led to the following conclusions: (1) in dilute aqueous solution (0·25—2·0 molar), the reaction $KCN + 2H_2O = H{\cdot}CO_2K + NH_3$ is of the first order; (2) the temperature-coefficient is normal, the values being about 2·26 at 100—110° and about 2·06 at 110—120°; (3) the presence of an excess of the products of the reaction

(NH_3 and HCO_2K), as well as of other salts and bases, has no appreciable effect on the rate of hydrolysis; (4) organic acids have a feeble, accelerating action; (5) alcohols, particularly glycerol, have a much more pronounced, accelerating action, which appears to depend on intermediate and side reactions. H. W.

The Kinetics of an Enzymatic Hydrolysis of Glycylglycine. KARL GUSTAV DERNBY (*Compt. rend. Lab. Carlsberg*, 1916, **11**, 263—295).—A quantitative study of the hydrolysis of glycylglycine by ereptase under varying conditions. The enzymatic decomposition of glycylglycine in an alkaline solution causes a diminution in the concentration of the hydrogen ions, the diminution becoming greater as the reaction proceeds. Glycylglycine has a greater dissociation constant (K_a) than glycine itself. The values found were: for glycine, $K_a = 1\cdot05 \times 10^{-10}$, $K_b = 1\cdot7 \times 10^{-12}$; for glycylglycine, $K_a = 3\cdot3 \times 10^{-9}$, $K_b = 0\cdot95 \times 10^{-11}$. The ereptase may be regarded as an amphoteric electrolyte, and its activity is notably influenced by variations in the hydrogen ion concentration of the medium. So long as this concentration remains constant and the optimum point is not passed, the scission of glycylglycine by means of ereptase is a unimolecular reaction, provided that the concentration of the enzyme with respect to the substance to be hydrolysed is sufficiently great for autolysis of the enzyme to be neglected. The dipeptide appears to exert a protective action on the enzyme, and thus the autolysis depends on the concentration of the dipeptide. Neither the products of hydrolysis nor the ions $K^{\cdot}$, $Na^{\cdot}$, Cl', Br', F', SO_4', or NO_3' in dilute solutions exert any influence on the velocity of the reaction. The ion ClO_3' tends to check the enzyme action, and the ion $(CN)'$ acts as a strong poison. W. G.

Chemical Dynamics of Autocatalytic Processes. I. Kinetic Theory of Autocatalysis and its Experimental Examination. JAN ZAWIDZKI (*Chem. Zentr.*, 1916, ii, 717—718; from *Anzeiger Akad. Wiss. Krakau*, [A], 1915, 275—318; *Abhand. Akad. Wiss. Krakau*, [A], 1916, **55**, 54—100).—The author discusses the development of the knowledge of autocatalytic phenomena, the discovery of chemical acceleration, the conception of autocatalysis, and of Ostwald's theory of molecular–kinetic autocatalytic action. The more recent experimental investigations on the velocity of autocatalytic reactions in homogeneous and heterogeneous systems and the autocatalytic character of biochemical processes are also described. The results of these investigations confirm, and to some extent extend, Ostwald's theory of autocatalytic acceleration.

A systematic analysis of the available investigations leads the author to the conclusion that the cases of autocatalytic acceleration which have been studied up to the present may be divided into two chief classes: I. Instances of simple autocatalysis in which the velocity of reaction may be expressed by the equations: (1) $dx/dt = k_2x^m(a-x)^n$, and (2) $dx/dt = k_2(a-x)^n/x^m$. II. In-

stances of compound autocatalysis for which the mathematical expressions are (3) $dx/dt=[k_1 \pm k_2(a-x)^m](a-x)^n$, and (4) $dx/dt=[k_1 \pm k_2x^m](a-x)^n$, where $(a-x)$=the concentration of the reacting substance at a definite period, x=the concentration of the reaction product, k_2=the velocity-coefficient of autocatalytic acceleration, and k_1=velocity-coefficient of catalytic acceleration.

H. W.

Chemical Dynamics of Autocatalytic Processes. II. Rate of Isomerisation of Triethyl Phosphite. JAN ZAWIDZKI and WILHELM STARONKA (*Chem. Zentr.*, 1916, ii, 718—719; from *Anzeiger Akad. Wiss. Krakau*, [A], 1915, 319—386; *Abhandl. Akad. Wiss. Krakau*, [A], 1916, **55**, 101—167. Compare preceding abstract).—According to Arbusov (A., 1910, i, 802), the isomerisation of triethyl phosphite under the catalytic influence of ethyl iodide occurs in accordance with the equations

$$EtI + P(OEt)_3 \longrightarrow {}^{Et}_{I}\!>\!P(OEt)_3 \text{ and}$$

$$ {}^{Et}_{I}\!>\!P\!<\!{}^{(OEt)_2}_{OEt} \longrightarrow {}^{Et}_{O}\!\geqslant\!P(OEt)_2 + EtI.$$

The authors have investigated the rates of these reactions at 95° and 85° by the dilatometric method, and find that the ethyl phosphinite produces an autocatalytic effect on the process. The reaction therefore presents an example of compound autocatalysis, and the velocity is expressed by the equation $dx/dt=(k_1+k_2x)(a-x)$.

Further study of the reaction has shown that the ethyl phosphinite only exercises an accelerating effect in the presence of ethyl iodide. The catalytic acceleration due to ethyl iodide and the autocatalytic action of the phosphinic ester are therefore closely connected, and the velocity of the isomerisation processes finds its quantitative expression in the following equation:

$$dx/dt=b/a\,.\,k(1+n'x/a)(1-x),$$

in which a=the original concentration of the ester, b=the concentration of the catalyst, x'=the proportion of isomerised ester, and $n'=a/0{\cdot}2a+0{\cdot}185b$. The values calculated from the second equation are in exact agreement with the experimental results, and the kinetic deductions derived from it can be quantitatively established. The process is therefore the first example of compound, coupled autocatalysis. A normal figure, 2·168, has been found for the temperature-coefficient of the velocity constants, k.

Preliminary experiments in different organic solvents have shown that the kinetic mechanism of the reaction varies with the chemical nature of the medium. In certain indifferent solvents, such as toluene, ethylene dibromide, propyl alcohol, and nitrobenzene, the reaction appears to be of the first order. In chemically active media, such as ethyl or methyl sulphate, on the other hand, reaction also occurs between the ethyl phosphite and the solvent.

Autocatalytic acceleration was not observed in any of the solvents so far investigated, the connexion between catalyst and autocatalyst thus appearing to be broken by the solvent. H. W.

Chemical Dynamics of Autocatalytic Processes. IV. Rate of Hydrolysis of Potassium Methyl Sulphate. JAN ZAWIDZKI and JANUSZ ZAYKOWSKI (*Chem. Zentr.*, 1916, ii, 719—720; from *Anzeiger Akad. Wiss. Krakau*, [A], 1916, 75—158. Compare preceding abstracts).—The authors have investigated the rate of hydrolysis of potassium methyl sulphate in aqueous solution which, at 105—115°, occurs in accordance with the equation $MeKSO_4 + H_2O = MeOH + KHSO_4$. Since the velocity of the reaction is accelerated by the potassium hydrogen sulphate which is formed, the reaction presents a typical instance of simple autocatalysis. The accelerating action of potassium hydrogen sulphate is actually due to the hydrogen ions formed by dissociation of the HSO_4' ions, and since the latter is a very weak acid, the concentration of the hydrogen ions is approximately proportional to the square root of the concentration of the potassium hydrogen sulphate at any given instant. The course of the reaction can therefore be expressed by the differential equation $dx'/dt = k_2\sqrt{a}\,.\,\sqrt{x'}(1-x')$, where a = initial concentration of potassium methyl sulphate and x' = the proportion which has undergone change after an interval of time, t.

The values deduced from the above equation are in complete harmony with the results of experiments on the hydrolysis of pure potassium methyl sulphate at various initial concentrations at 105° and 115°, whilst they also agree satisfactorily with the experimental results obtained in the presence of an excess of the products of the reaction (MeOH or $KHSO_4$) or of neutral potassium salts (KCl and KNO_3). The following regularities are apparent: (1) addition of methyl alcohol exercises a slight retarding effect on the rate of hydrolysis of the ester salt; (2) neutral salts have a feebly accelerating action; (3) normal potassium sulphate has a powerful retarding action, since the dissociation equilibrium, $HSO_4' \rightleftharpoons H^{\bullet} + SO_4''$, is displaced towards the left side. This action of potassium sulphate is approximately proportional to the cube root of its concentration.

Strong mineral acids (HCl and H_2SO_4) have a very marked, accelerating action on the rate of hydrolysis of potassium methyl sulphate, which, in this case, is mathematically expressed by the equation $dx'/dt = k_3/\beta(m+x')(1-x')$, where $\beta = b/a$, the relationship of the concentration of the added acid to the initial concentration of the ester salt, $m = \beta + a\beta^2/s$, and s is the dissociation constant of the hydrosulphate ion. Weak acids, such as formic and acetic acids, slightly increase the initial rate of hydrolysis, and subsequently have a slight retarding effect. The salts of these weak acids, and also the free bases (KOH), completely alter the kinetic mechanism of the change. In their presence, the hydrolysis of potassium methyl sulphate commenced fairly rapidly; a transitory period of equilibrium then occurred, after which the action became complete in autocatalytic time.

The temperature-coefficient of the velocity constants of the hydrolysis of potassium methyl sulphate in the interval of temperature, 105—115°, is 2·75. H. W.

A General Twin Series of Varieties of Atoms. A. van den Broek (*Physikal. Zeitsch.*, 1916, **17**, 579—581).—An attempt to show the existence of relations between the different kinds of atoms, which involves the assumption that the ordinary elements are in many cases mixtures of chemically similar, but not identical, varieties of atoms. H. M. D.

Inorganic Chemistry.

Preparation of Hydrogen from Formates and from Carbon Monoxide. G. Gianoli (*Ann. Chim. Applicata*, 1916, **6**, 256—257).—Polemical against Levi and Piva (A., 1916, ii, 525).

T. H. P.

The Oxy-Ammonia Flame. D. L. Hammick (*Chem. News*, 1916, **114**, 285. Compare Hodgkinson and Lowndes, A., 1888, 1244).—When an oxy-ammonia flame is obtained in an ordinary blowpipe burner, the characteristic peach-coloured flame is obtained with a small supply of oxygen. On increasing the pressure of oxygen, a livid-white central cone surrounded by a pale peach-coloured luminescent sheath is produced. If the flame is allowed to play on water or ice, nitrates and nitrites can be easily detected in solution.

W. G.

The Action of Nitric Oxide on Metallic Peroxides Suspended in Water. Barun Chandra Dutt and Surya Narayan Sen (*J. Proc. Asiatic Soc. Bengal*, 1914, [N.S.], **10**, 287—291).—When nitric oxide is passed into a suspension of lead peroxide in water, a mixture of lead nitrite and nitrate is formed (compare Sabatier and Senderens, A., 1892, 1151, 1271), the nitrate being formed by the oxidation of a portion of the nitrite by the excess of lead peroxide. With barium peroxide in water, nitric oxide yields only barium nitrite.

W. G.

The Molecular Weight of Ortho- and Pyro-phosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 139—142. Compare A., 1915, ii, 446; this vol., ii, 23).—Orthophosphoric acid is partly converted into the pyro-acid when kept in a desiccator over phosphoric oxide, or even over sulphuric acid. Orthophosphoric acid has the simple molecular weight in sulphuric acid solution, and if the free acid had the same constitution, it might be expected that the pyro-acid would also be formed on dissolving in sulphuric acid, but this is not the case. Ethyl and methyl orthophosphates have vapour densities corresponding approximately with the simple formulæ. The pyrophosphoric acid molecule is probably simple.

C. H. D.

Silicon and its Position in the Thermoelectric Series. II. FRANZ FISCHER and ERNST BAERWIND (*Zeitsch. anorg. Chem.*, 1916, **97**, 56—72. Compare A., 1913, ii, 550).—The difference between the positive and negative varieties of silicon has been attributed to the presence of oxygen in the former. Attempts have now been made to confirm this by analysis. Total silicon is estimated by the fusion method and free silicon by measuring the hydrogen evolved on treatment with potassium hydroxide. It is necessary to grind very finely, and this grinding causes an oxidation of a part of the silicon. The same effect is obtained when a mortar of silicon is used instead of agate. Finely ground silicon oxidises to a notable extent at 210°, so that the oxidation during grinding may be caused by local rise of temperature, aided by the continual formation of fresh surfaces. It has not been found possible to estimate accurately the percentage of oxygen in silicon, even when the substance is dissolved in fused potassium hydroxide in a silver flask, without previous grinding.

The sign of the thermoelectric effect is quite independent of the iron content. The effect is also not due to the presence of aluminium in the positive variety. It is considered that oxygen in solid solution and in very small quantity is responsible for the change of sign. C. H. D.

Oxidation of Carbon by Air at Low Temperatures in Presence of Iron and Other Metals. A. P. LIDOV (*Reprint.* pp. 11. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260). —Experiments have been made on the oxidation of finely divided carbon in the air at low temperatures in the presence of lead, nickel, iron, and other metals. Charcoal activated with lead does not lose its activity for a very long time, whereas that activated with nickel or iron loses it rapidly, probably because the metal, precipitated on the surface of the charcoal, becomes converted into its higher oxide. The density of the gas giving a precipitate with barium hydroxide solution, and obtained by the oxidation of carbon activated by means of lead, is always less than that obtained from carbon activated with nickel or iron, and is, on the average, very near to the density of oxan. H. W.

Combination of Carbon and Nitrogen at the Ordinary Temperature. A. P. LIDOV (*Reprint.* pp. 4. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260).—In presence of catalytic iron, the first action of air (free from carbon dioxide) on carbon in the cold consists in the gasification of the solid carbon, with formation of the simplest nitrogen–carbon compounds, namely, active α- and inert β-monocyanogen. The oxygen of the air does not take part in the initial stage of the process; this result agrees with those of the author's earlier experiments with pure oxygen in the cold, which showed that, under such conditions, carbon does not undergo the slightest gasification. In the second phase of the process, the α-monocyanogen is oxidised to the stable α-oxan, OCN, and possibly to peroxan, O_2CN. H. W.

Carbon Dioxide from Natural Limestones. A. P. Lidov (*Reprint*, pp. 35. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260).—A number of samples of calcspar, aragonite, friable limestones, such as chalk, dense limestones, such as marble, etc., have been decomposed with acid and the density of the evolved gas measured. Variable results were obtained, the values for the gas from calcite being exceptionally low. In explanation of this phenomenon, it is suggested that many limestones contain a more or less considerable proportion of α-oxan, OCN, in addition to the combined carbon dioxide; owing to its ease of formation, α-oxan may be widely distributed. H. W.

Separation of Sodium and Potassium Salts. Spar Chemical Co. (U.S. Pat., 1194465; from *J. Soc. Chem. Ind.*, 1916, **35**, 1261).—To a solution containing, for example, sodium sulphate (90 parts) and potassium sulphate (10 parts), sodium chloride is added in equimolecular proportion to the potassium salt, and the liquid is evaporated until sufficient sodium sulphate has separated to leave an amount of potassium chloride in solution equal to 40% of the total dissolved salts. The mother liquor is then treated with sodium nitrate (in amount equimolecular to the potassium chloride), and the solution is evaporated, whereby sodium chloride and sulphate separate from the hot liquid; these are used for the treatment of a new batch of the mixed sulphates. The potassium nitrate left in the mother liquor is crystallised, leaving sodium chloride and nitrate and about 15% of potassium nitrate in solution; it is separated, redissolved in water, added to the original solution of mixed sulphates (so that equimolecular proportions of sodium sulphate and potassium nitrate are present), and, on evaporating, potassium sulphate separates, which is removed and washed with hot water. The wash water, containing chiefly sodium nitrate, together with the mother liquor from the potassium nitrate crystallisation, is added to the solution containing 40% of potassium chloride instead of fresh sodium nitrate. The reagents are thus used repeatedly, the only materials separated being sodium sulphate from the first evaporation and potassium sulphate from the last. H. W.

The Double Salts Formed by Sodium and Potassium Carbonates. J. W. Bain and C. E. Oliver (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 65—66).—The production of pure potassium carbonate from the ash of seaweeds, wood ashes, and the residues from sugar factories is rendered difficult by the formation of the double salt, $K_2CO_3,Na_2CO_3,12H_2O$. According to dilatometric observations, this double salt decomposes at 35° in accordance with the equation

$$3(K_2CO_3,Na_2CO_3,12H_2O) = 2K_2CO_3 + K_2CO_3,3Na_2CO_3,10H_2O + 26H_2O.$$

The new double salt thus formed appears to decompose at about 130°. H. M. D.

The Dehydration of Sodium Hydrogen Phosphate. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 147—148. Compare *ibid.*, 1914, **88**, 135).—Sodium hydrogen phosphate is dehydrated at 250°±2°, even in a very moist atmosphere. This is probably the melting point of the salt. By sealing the salt with water in a glass tube, the volumes being known, the relation between the vapour pressure and temperature may be determined. Fusion is not observed in this case, although pyrophosphate is formed. The salt may be partly dehydrated and converted into pyrophosphate by heating with sulphuryl chloride. C. H. D.

Reduction of Silver Chloride and Lead Chloride. A. Gawalowski (*Chem. Zentr.*, 1916, ii, 723; from *Österr. Chem. Zeit.*, **19**, 150—151).—Precipitated silver chloride is reduced to metallic silver by means of zinc in a few days. $AgNH_3$ gives with zinc and mercury a silvery-grey, dendritic silver tree, whilst with zinc, copper, tin, and mercury it yields at first black, dendritic deposits, which after a time become converted into silver-white dendrites. Scaly, crystalline leaflets of lead are formed by the reduction of aqueous lead chloride by zinc, whilst in the presence of ammonia the lead is precipitated in powdery, black microcrystals. If the deposit containing ammonia is acidified with dilute sulphuric acid, the odour of nitrous acid is observed, and lead is almost instantaneously precipitated in dendritic crystals. H. W.

Silver Peroxynitrate. Mortimer J. Brown (*J. Physical Chem.*, 1916, **20**, 680—700).—When an aqueous solution of silver nitrate is electrolysed between insoluble electrodes, a black substance separates at the anode under certain conditions. This substance has been frequently examined, but its composition is still doubtful. It appears to be decomposed by the nitric acid in the solution as soon as the crystals are detached from the anode.

In the further investigation of the compound, experiments have been made with an electrolytic apparatus which permits of an accurate measurement of the current yield. In this apparatus, the solution is continuously circulated through the decomposition cell, and the decomposing action of the nitric acid is avoided by neutralising the acid by the action of suspended silver carbonate.

From experiments with 5% and 20% silver nitrate solutions and varying current strengths, the silver content of the anode deposit was found to vary between 79·03% and 79·82%, the average being 79·37%. The ratio of the anode deposit to copper deposited in the same circuit varied from 2·69 to 2·98.

These results agree with the formula $2Ag_3O_4,AgNO_3$, which requires 79·9% for the silver content and 2·97 for the coulometer ratio. This is one of the several compounds which have been suggested by the results of previous experiments. The small discrepancies between the calculated and observed silver contents and coulometer ratios are probably due to secondary disturbances.

The current yield numbers show that 10 faradays are required for the deposition of 1 gram-molecular weight of the silver peroxynitrate. H. M. D.

Plaster of Paris. L. A. KEANE (*J. Physical Chem.*, 1916, **20**, 701—723).—The literature relating to plaster of Paris has been examined, and some experiments are described which show that a dead-burned plaster may be transformed into a plaster which sets fairly rapidly with water by grinding so as to obtain particles of very small size. H. M. D.

The Melting Point and Heat of Fusion of Glucinum. G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1916, **97**, 1—6).—Glucinum, prepared electrolytically from sodium glucinum fluoride, is pressed into pastilles and fused in a magnesia tube in hydrogen. The product contains 99·5% Gl, the principal impurity being the carbide. Heating and cooling curves give the value $1278° \pm 5°$ for the melting point. An approximate determination of the heat of fusion by comparing the duration of the arrests when equal volumes of gold and glucinum are cooled under similar conditions gives 277 cal. per gram, whilst Crompton's rule, atomic weight $\times$ heat of fusion $\div$ absolute temperature of fusion $= 2$, gives the value 341. Glucinum has the largest heat of fusion of any metal, corresponding with its high melting point and low atomic weight.

C. H. D.

The Alloys of Glucinum with Aluminium, Copper, Silver, and Iron. G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1916, **97**, 6—40).—Glucinum and aluminium are miscible in the liquid state and do not form a compound. The freezing-point curve has two branches, with a eutectic point at 644° and 4 atomic % Gl. Solid solutions are only formed at the glucinum end of the series up to 3 atomic %. The sections may be etched with dilute sodium hydroxide. For analysis, the quantity available being small and the separation difficult, it is advisable to dissolve in hydrochloric acid and measure the volume of hydrogen evolved, as glucinum gives off about twice as much as aluminium, equal weights being taken, and the composition may then be found by interpolation.

It has not been found possible to alloy glucinum and magnesium, as the latter boils below the melting point of the former. It is not certain whether the metals are miscible or not.

The alloys with copper are complicated. The freezing point of copper is first lowered, solid solutions being formed up to 10 atomic % Gl, and beyond this the liquidus and solidus, which are separated by a very small interval, have an unusual form, passing through a minimum and a point of inflexion. This β-solution breaks up at a lower temperature, there being a eutectoid point at 575° and 31 atomic % Gl. There is a short ascending branch corresponding with the separation of a γ-solution, and then the freezing-point

curve rises to a maximum at the composition $CuGl_3$, beyond which it has not been possible to follow the alloys. The δ-solution contains from 70 atomic % Gl upwards. The transformation of β into α and γ is confirmed by quenching experiments. The eutectoid has a structure very like that of the pearlite of steel. The compound $CuGl_3$ is reddish-grey. The alloys may be dissolved in nitric acid for analysis, and the copper estimated by electrolysis.

Silver and glucinum give a simple eutectiferous system, the eutectic point being at 878° and 16 atomic % Gl. Solid solutions are only formed to the extent of about 8 atomic % at the glucinum end of the series. A transformation point at 748° has been observed, and as pure glucinum is not allotropic, it is suggested that a compound may be formed. The alloys increase in hardness and diminish in ductility as the glucinum increases.

The alloys with iron have been examined up to 21% Gl by weight. There is a eutectic point at 1155° and 38·4 atomic % Gl, the region of solid solutions extending to 29%. The β-α-transformation of iron is lowered by glucinum, becoming constant at 650°. The compound, which may have the formula $FeGl_2$, is darkened by sodium hydroxide. C. H. D.

Action of Magnesium on Solutions of Potassium Chloride. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 2594—2607).—The action of magnesium on water and solutions of potassium chloride has been examined in the following manner. The rate has been determined at which hydrogen is evolved from (*a*) distilled water, (*b*) conductivity water, and (*c*) solutions of potassium chloride of concentrations varying from N to $0·1N$, when strips of magnesium of uniform dimensions are immersed in them. It is shown that the rate of gas evolution is greatly increased by the presence of potassium chloride, but the increase is not proportional to the concentration of the solution. The potential difference between magnesium and solutions of potassium chloride has also been determined. The potential decreases with time in a given solution, and also decreases with decreasing concentration. The hydrogen-ion concentration, both in pure water and in solutions of potassium chloride in which magnesium is immersed, has also been determined. Finally, the concentration of potassium chloride in the solutions after the experiments was determined. The evidence obtained from the experiments has led to the conclusion that the reaction between water and magnesium is to be represented by the equation $Mg + 2H_2O = Mg(OH)_2 + H_2$, and that the presence of the dissolved salt merely accelerates the reaction catalytically. J. F. S.

The Colour of Magnesium Pyrophosphate obtained by Calcining $MgNH_4PO_4,6H_2O$. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1916, **97**, 149—160).—The grey or black colour often seen in ignited magnesium pyrophosphate is attributed by S. Karaoglanoff (*Jahrb. Univ. Sofia*, 1910—11, **7**) to traces of organic matter accidentally introduced during the precipitation and filtration, but

according to this author the coloration is only observed when the pyrophosphate has the dense form which results from incandescence during ignition. Reagents which remove the coloration do so by altering the texture of the precipitate, allowing oxygen to enter and oxidise the carbon.

The colour depends on the water of crystallisation present. The moist, crystallised salt with $6H_2O$ yields a snow-white residue on ignition, but if kept for some weeks over phosphoric oxide, it becomes grey when ignited. There is no appreciable difference of weight between the white and coloured residues, but the grey pyrophosphate is less readily soluble in hot dilute nitric acid than the white variety. The addition of filter-paper fibres to $MgNH_4PO_4,6H_2O$ causes the precipitate to darken on ignition, but if moistened two or three times with water, the residue is white. Dark residues are often obtained even when asbestos is used for filtering. Secondary changes often occur in the precipitation and ignition of the phosphate. The various methods of decolorising the residue give the same results if precautions are taken against loss. Moistening with water and adding a few crystals of ammonium nitrate removes the colour rapidly and completely. C. H. D.

Atomic Weight of Lead of Radioactive Origin. THEODORE W. RICHARDS and CHARLES WADSWORTH, 3rd (*J. Amer. Chem. Soc.*, 1916, **38**, 2613—2622. Compare A., 1914, ii, 653; 1916, ii, 250).—A further set of atomic-weight determinations of lead separated from radioactive minerals. Four sets of results have been obtained from material of different origins, and the following mean results obtained: ordinary lead, 207·18; radioactive lead (Colorado), 207·00; radioactive lead (Australia), 206·34; radioactive lead (obtained from bröggerite, Norway), 206·12; and radioactive lead (obtained from cleveite from Langesund, Norway), 206·08. The most carefully selected sample gave the lowest result, and consequently the authors assume that the higher results obtained from other samples are due to accidental admixture of ordinary lead. As in previous work, no new lines were found either in the ultra-violet or visible spectrum of any of these samples. Hence the atom of lead may be supposed to have a dual structure. Each sample, except the ordinary lead, was radioactive, but the magnitude of the radioactivity seemed to bear no relation to the lowering of the atomic weight. J. F. S.

Some Reactions Involved in Secondary Copper Sulphide Enrichment. E. G. ZIES, E. T. ALLEN, and H. E. MERWIN (*Economic Geology*, 1916, **11**, 407—503).—Copper sulphate solutions react with natural sulphides, a part of the copper being precipitated, this being the process which is concerned in the secondary enrichment of sulphide deposits. The minerals are used either in the form of lumps, so that the colour of the product may be determined, or more often in powder. In the latter case, the powder is sifted through silk bolting cloth, only that part being

taken which passes through a cloth with 125 meshes to the linear inch and is retained by a 200 mesh. The finest flour, which adheres to the particles in sifting, is removed by washing with alcohol. The minerals after the experiment are examined microscopically and analysed.

The reactions are carried out at the ordinary temperature in special glass containers in a shaking apparatus, and at higher temperatures in sealed tubes of Jena glass or silica, heated vertically in an oil-bath. When artificial sulphides are to be tested, they are prepared by precipitation and washing, and are dried and heated in hydrogen.

Pyrites is altered to covellite and chalcocite with cupric sulphate solutions. Chalcopyrite and bornite undergo the same change, whilst pyrrhotite is altered to chalcopyrite, and probably to bornite. The order of stability is: chalcopyrite, covellite, chalcocite, the last being the most stable of all, although even it is slowly altered, yielding metallic copper and sulphuric acid. The intermediate products, chalcopyrite and covellite, are most likely to be obtained when a large surface of the original sulphide is exposed to a dilute solution of cupric sulphate. Increased temperature accelerates the reactions without greatly altering their nature, but secondary reactions, such as the formation of cuprous sulphate and hydrolysis to hæmatite, are more marked at higher temperatures. Cuprous sulphate appears to accelerate the reactions. An increased concentration of sulphuric acid retards the above reactions. A reversal of the enrichment reactions has not been observed. Galena is more reactive than any other of the sulphides examined. The enrichment of galena, blende, pyrrhotite, and bornite is accelerated by the presence of sulphuric acid. C. H. D.

Investigations at High Temperatures. X. Aluminium and Carbon. OTTO RUFF and ERNST JELLINEK (*Zeitsch. anorg. Chem.*, 1916, **97**, 312—336).—Aluminium carbide prepared by heating the metal with carbon contains much nitride. Carbon, prepared by crushing the most strongly heated portions of a carbon resistance tube and boiling with hydrochloric acid, contains only 0·08% of ash, and may be heated with aluminium in a carbon crucible in an atmosphere of hydrogen. After half an hour at 2000°, the mass is compact and dark orange in colour. It contains some aluminium, or a carbide rich in aluminium.

For analysis, the carbide is heated with 4*N*-sulphuric acid, and the evolved gases burnt in a copper oxide tube. The insoluble residue in the flask is collected on a Gooch filter, and dried at 300° to remove sulphuric acid. It consists chiefly of carbon and alumina. The filtrate is used for the estimation of aluminium, iron, and silicon in one portion, another portion being taken for the estimation of nitrogen as ammonia. Small quantities of sulphur are estimated in a fresh quantity of carbide by the evolution of hydrogen sulphide. The highest content of aluminium carbide, Al_4C_3, in the product is 83%, with 6·7% of nitride, the remainder including insoluble matter, iron, silicon, and aluminium.

The highest proportion of methane in the gas evolved with hydrochloric acid is 97·5%, the remainder being hydrogen, but as much as 19·2% of hydrogen has been obtained.

Aluminium carbide partly melts, forming aluminium and graphite, a little above 2200°. The proportion of carbon in the vapour increases with the pressure and with the temperature. The analyses are made by the method employed for other carbides, the loss of weight of the solid components being determined (Ruff and Bormann, A., 1915, ii, 461). The impurities are allowed for in the calculation. Aluminium carbide is more stable in the form of vapour than any of the other carbides examined (manganese, cobalt, iron, and nickel). C. H. D.

The Solubility of Aluminium Hydroxide in Solutions of Ammonia and Ammonium Salts. E. H. ARCHIBALD and Y. HABASIAN (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 69—70).—The solubility of aluminium hydroxide in ammonia increases at first with the strength of the ammonia solution, reaches a maximum, and then decreases. These relations are supposed to be connected with the formation of a more crystalline modification of aluminium hydroxide in contact with the concentrated ammonia. In presence of ammonium chloride or nitrate, the solubility of the hydroxide is considerably decreased. The addition of potassium nitrate increases the solubility to a marked extent. H. M. D.

Oxidation-reduction Reactions without the Addition of Acid. III. Ferrous Chloride and Potassium Permanganate. A New Method for the Preparation of Colloidal Hydrated Ferric Oxide. MARKS NEIDLE and JOHN N. CROMBIE (*J. Amer. Chem. Soc.*, 1916, **38**, 2607—2613. Compare A., 1916, ii, 603).—Solutions of ferrous chloride and ferrous sulphate have been titrated with solutions of potassium permanganate without the addition of acid. It is shown that the stoicheiometric relationships are the same as in the oxidation in the presence of acid. In the oxidation of ferrous chloride, it is shown that the collateral oxidation of the chloride ion is practically avoided by adding the permanganate gradually and stirring the solution vigorously. The products of reaction with ferrous chloride are the chlorides of potassium, manganese, and ferric iron, together with colloidal hydrated ferric oxide, whilst with ferrous sulphate the corresponding sulphates are formed, and also hydrated ferric oxide, which is precipitated by the sulphion. One gram-equivalent of potassium permanganate dissolved in about 600 c.c. of water was slowly added to 1 gram-equivalent of ferrous chloride dissolved in a litre of water, and the resulting clear, deep brownish-red solution diluted to 2 litres. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension separated. Until the latter stage is reached, dialysis yields a perfectly clear, brownish-red sol of hydrated ferric oxide. After the suspension has settled, dialysis gives a hydrated

ferric oxide sol which is slightly turbid in reflected light, but perfectly clear in transmitted light. J. F. S.

The Hydrolysis of Iron Ammonium Alum. WILLIAM NORMAN (T., 1916, **109**, 1331—1339).—The precipitate which separates from solutions of ferric ammonium alum on keeping is found to have the composition $2Fe_2O_3,SO_3$. The colours of iron alum solutions alone and in the presence of sulphuric acid, ammonium sulphate, sucrose, potassium chloride, and alcohol have been measured by means of a Duboscq colorimeter, and are shown to be in agreement with the supposition that the colour is due to the presence of a soluble form of the basic sulphate of the composition given above.

The white precipitate obtained on adding concentrated sulphuric acid to a solution of iron ammonium alum is found to be the anhydrous alum. The densities and apparent molecular solution volumes of iron ammonium alum solutions of varying concentrations at 32·5° have been determined. T. S. P.

Cobaltammines. I. Various Ionisation Types as Determined by the Freezing Point Lowering in Aqueous Solution, together with Conductivity Measurements. WILLIAM D. HARKINS, R. E. HALL, and W. A. ROBERTS (*J. Amer. Chem. Soc.*, 1916, **38**, 2643—2658).—The authors have prepared the following cobalt derivatives and have measured the conductivity and lowering of the freezing point of solutions of these salts: hexamminecobalt chloride, nitropentamminecobalt chloride, chloropentamminecobalt chloride, dinitrotetramminecobalt chloride, dinitrotetramminecobalt nitrate, cobalttrinitrotriammine, potassium tetranitrodiamminecobaltate, ammonium tetranitrodiamminecobaltate, and sodium cobaltic nitrite. The freezing point determinations were made in fairly dilute solutions, and the temperature changes measured by means of a fifty-junction differential thermo-element of copper and constantan wire. In each case the freezing point lowerings are compared with those of salts of similar and known ionic type. It is shown that hexamminecobalt chloride, $[Co(NH_3)_6Cl_3]$, is of the same type as lanthanum nitrate–tetraionic; nitropentamminecobalt chloride,

$$[NO_2(NH_3)_5CoCl_2],$$

and chloropentamminecobalt chloride, $[ClCo(NH_3)_5Cl_2]$, are similar to cobalt chloride, tri-ionic in character; dinitrotetramminecobalt chloride and nitrate, $[(NO_2)_2Co(NH_3)_4Cl]$, are similar to sodium iodate–di-ionic salts; trinitrotriamminecobalt is non-ionic. Potassium tetranitrodiamminecobaltate, $[(NO_2)_4Co(NH_3)_2K]$, and ammonium tetranitrodiamminecobaltate, $[(NO_2)_4Co(NH_3)_2NH_4]$, are like potassium iodate, and evidently di-ionic; sodium cobaltic nitrite, $[(NO_2)_6CoNa_3]$, is tetraionic. The degree of ionisation and the ratio $\Delta t/N$ is calculated for each concentration in each case. The electrical conductivity of the above-mentioned compounds, as well as that of magnesium sulphate, have been determined at 0° and 25° for a number of concentrations, and the degree of ionisa-

tion calculated. The results show that the type of each salt is that assumed for it by Werner, but the freezing-point measurements do not agree well with those of Werner. There is a large discrepancy, except in the case of trinitrotriamminecobalt, between the present results and those of Petersen (A., 1897, ii, 302; 1902, ii, 126), often amounting to as much as 100%. For these discrepancies the authors are unable to offer any explanation.

J. F. S.

The Occlusion of Iron by the Ammonium Phospho-Molybdate Precipitate. E. H. ARCHIBALD and H. B. KEEGAN (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 67—68).—The factors which influence the occlusion of iron by ammonium phosphomolybdate have been examined. In the case of dilute solutions, the amount of occluded iron is independent of the quantity of iron in the solution, but in more concentrated solutions it increases with the quantity of dissolved iron. For solutions of the same iron concentration, the quantity of occluded iron increases somewhat more rapidly than the concentration of the phosphoric acid. The dilution of the solution has no appreciable influence on the amount of occluded iron when the quantities of iron and phosphoric acid remain the same.

The iron is occluded at the time of precipitation, and is not removed by washing. It is suggested that a definite chemical compound is formed. H. M. D.

Investigations at High Temperatures. IX. The Preparation of Articles of Zirconia. OTTO RUFF and GEORG LAUSCHKE (*Zeitsch. anorg. Chem.*, 1916, **97**, 73—112. Compare A., 1914, ii, 474).—The fusibility of mixtures of zirconia with other oxides has been determined, using a carbon tube furnace, the atmosphere of the furnace being under a low pressure. Zirconia containing 98·73% ZrO_2, the remainder being silica and iron oxide, melts at $2563° \pm 10°$, the temperature of the previous shrinking operation being without influence. Thoria has not been melted in the reducing atmosphere of this furnace, the oxide cracking and giving off fumes at 2450° without fusion. Glucina, alumina, yttria, and thoria are suitable for addition to zirconia, causing little volatilisation, whilst magnesia causes fuming and silica lowers the melting point excessively.

For the preparation of crucibles, the addition of 1% of alumina is recommended for use at 2000°, or 1% of thoria at 2200°, and from 1 to 3% of yttria at 2400°. The addition of larger quantities increases the porosity and has no advantage. Both the porosity and the contraction vary with the temperature of firing. Magnesia and glucina reduce the porosity.

Pure zirconia is readily soluble in hydrofluoric acid at 25°. Zirconium and thorium may be separated in this way, the oxide of the latter remaining insoluble. Details for the preparation and separation of thorium and zirconium fluorides are given.

C. H. D.

Ammoniacal Derivatives of Platinous Nitrite. LEO ALEXANDROVITSCH TSCHUGAEV and STANISLAV STANISLAVOVITSCH KILTINOVIC (T., 1916, **109**, 1286—1295).—Compounds corresponding with the general formula $Pt2NH_3X_2$ or $Pt2AX_2$ (A = amine) are formed by the action of ammonia or of amines on complex salts of the type $[PtX_4]M_2$, but hitherto it has not been ascertained if they have in all cases the same *cis*-configuration. This question, and, more generally, the study of the ammonia compound of platinous nitrite, have now been taken up by the authors.

The addition of ammonia to a cold solution of potassium platinonitrite gives a precipitate of very fine and nearly colourless crystals of the formula $[(NO_2)_2Pt(NH_3)_2]$. Comparison of the physical properties of this substance with those of the known isomeric compounds shows that it consists of *cis*-dinitrodiamminoplatinum. Its constitution was further proved by showing that the compound *cis*-$[Cl_4Pt(NH_3)_2]$ is produced on boiling with concentrated hydrochloric acid, and this can be further reduced to *cis*-$[Cl_2Pt(NH_3)_2]$ by means of oxalic acid. The *cis*- and *trans*-dinitrodiamminoplatinum differ from each other in that the former, on treatment with potassium hydrogen oxalate, readily gives the yellow complex salt, $K_2[Pt(NO_2)_2(C_2O_4)]$, from which the salt,

$$[Pt4NH_3][Pt(NO_2)_2(C_2O_4)],$$

is obtained as orange-yellow needles by precipitation with Reiset's Base I.

Both *cis*- and *trans*-dinitrodiamminoplatinum dissolve in dilute aqueous ammonia on heating, and from the solution potassium platinochloride precipitates nitrotriamminoplatinous platinochloride, $[NO_2Pt(NH_3)_3]_2PtCl_4$, as small, flesh-coloured, glistening plates. The corresponding nitrite, $[NO_2Pt(NH_3)_3]NO_2$, can also be obtained, from which, by appropriate reactions, the *platinobromide*, $[NO_2Pt(NH_3)_3]_2PtBr_4$, deep violet needles, and the *platinonitrite*, $[NO_2Pt(NH_3)_3]_2Pt(NO_2)_4$, pale yellow needles, can be prepared. The nitrite readily loses one molecular proportion of ammonia, giving rise to *trans*-dinitrodiamminoplatinum. T. S. P.

Mineralogical Chemistry.

Lorettoite, a New Mineral. ROGER C. WELLS and ESPER S. LARSEN (*J. Washington Acad. Sci.*, 1916, **6**, 669—672).—The new mineral occurs as honey-yellow, slabby masses at Loretto, Tennessee. It has an adamantine lustre and a bladed structure with a perfect cleavage along the blades. D 7·39 is perhaps low, owing to the presence of minute gas cavities, arranged along planes at right angles, which impart a cloudiness to the material. The substance is optically uniaxial and negative ($\omega_{Li} = 2{\cdot}40$, $\epsilon_{Li} = 2{\cdot}37$), and prob-

ably tetragonal. Hardness, 3; fusibility, 1. It is readily soluble in hot dilute nitric acid. Analysis by R. C. Wells of nearly pure material gave:

PbO.	Cl.	P_2O_5.	CaO.	MgO.	Al_2O_3.	ZnO.	CO_2.	H_2O.	Insol.	Total, less O for Cl.
93·98	3·98	0·11	0·48	0·56	0·08	0·31	0·20	0·03	0·58	99·41

A second determination of the chlorine gave 4·09%. A specimen in the collection of the University of California, labelled as "massicot," but of unknown locality, has D 7·65 and optical characters identical with those of lorettoite; this contains chlorine, 4·94%. These results approximate to the formula $6PbO,PbCl_2$.

L. J. S.

Cristobalite. HENRY LE CHATELIER (*Compt. rend.*, 1916, **163**, 948—954).—The author has found crystals of cristobalite in a mass of "quinquet," used for making miner's lamp glasses, in siliceous bricks from the dome of a glass furnace, and in the residues from the manufacture of siliceous bricks which had been heated at 1700°. The formation is explained on the grounds that the quartz dissolves in the fused mass, in some cases at 800°, giving a saturated solution which, maintained at the same temperature for some days, deposits cristobalite, which is less soluble. In the same way, cristobalite may become converted into tridymite, but the process is much slower. The author does not agree with Fenner (compare A., 1913, ii, 133) that from 1480—1780° cristobalite is the stable form and not tridymite, as he failed to get any conversion of tridymite when it was heated at 1700° for some time.

W. G.

The Separation and Thermal Metamorphosis of the Zechstein Salts: Bischofite, Kainite, and Blödite. M. ROZSA (*Zeitsch. anorg. Chem.*, 1916, **97**, 41—55. Compare A., 1916, ii, 257).—The view of Jänecke, that carnallite has been formed by the fusion of a layer of bischofite, which has then penetrated into the lower layers of hard salt and langbeinite, is untenable. Kieserite and carnallite must have been formed by the action of mother liquors rich in magnesium chloride on the solid salts during the drying process. The author's previous conclusions are maintained.

C. H. D.

Analytical Chemistry.

The Sulphonephthalein Series of Indicators and the Quinone-Phenolate Theory. H. A. LUBS and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2772—2784. Compare A., 1908, i, 423, 652, 653; 1909, i, 650).—The authors have examined a number of sulphonephthalein compounds prepared by Lubs and

Clark (A., 1916, ii, 44, 570), and examined by White (*Science*, **42**, 101), determining in each case the P_H range and the number of molecules of alkali required per molecule of indicator to raise the P_H value sufficiently to give the intense colour change characteristic of each indicator. The sulphonephthaleins, having no negative groups in the phenol residues, give yellow or orange solutions, their colours and conductivities showing that they exist largely in the quinoidal form. They are "self-indicators" requiring from 0·85—0·98 mol. of alkali before the intense colour change due to the dibasic salt is observed. The monobasic sulphonic acid salt has practically the same colour as the almost completely ionised, free acid. The introduction of negative groups into the benzene–sulphonic acid residue increases the affinity constant of this group, but does not appreciably alter that of the phenol group. All these facts and the experimental data support the quinone–phenolate theory of Acree (*loc. cit.*). The free sulphonephthaleins and their monobasic salts give absorption spectra containing a yellow band characteristic of the quinones. This disappears, and a deep red band appears when the dibasic salt is formed, indicating that the quinone group as such disappears, owing to the formation of a complex quinone–phenolate group.

By substituting bromo-, nitro-, methyl, *iso*propyl, amino-, and other groups in the benzenesulphonic acid group, and in the phenol residue, it is possible to change the ionisation constants of the sulphonic acid and phenol groups, and hence prepare a series of indicators having a wide range of sensibility of hydrogen ions.

W. G.

Control of Water Supplies which have been Chlorinated. Le Roy (*Ann. Falsif.*, 1916, **9**, 339—345).—The iodide–starch reaction is the most sensitive of many reactions which have been proposed for the detection of active chlorine in water. The water to be tested should, however, be cooled to 10° or lower before the reagent is added; at this temperature, 0·00006 gram of chlorine per litre of water will give a reaction, whilst at 20°, 0·0001 gram of chlorine cannot be detected. A reagent which will detect as little as 0·00002 gram of chlorine per litre may be prepared by dissolving 1 gram of hexamethyltri-*p*-aminotriphenylmethane in 10 c.c. of dilute hydrochloric acid (1 : 1), diluting the mixture to 100 c.c., adding animal charcoal, and filtering it; this reagent, which gives a violet coloration with chlorine, is more sensitive at 20° than at 10°, and is less affected by nitrites than is the iodide–starch solution. It does not give a coloration with hydrogen peroxide. A description is given of a colorimeter for use in the estimation of chlorine by means of this reagent. W. P. S.

Reactions for Distinguishing between Perchlorates, Periodates, Percarbonates, Persulphates, and Perborates. A. Monnier (*Ann. Chim. anal.*, 1916, **21**, 237—240).—The solution to be tested should be free from heavy metals, vanadates, tungstates, molybdates, dichromates, and ferricyanides. *Per-*

borates and percarbonates.—The two salts give respectively the usual reactions for boric acid, carbon dioxide, and hydrogen peroxide, and yield a blue coloration when their solution is treated with potassium dichromate and dilute sulphuric acid. If a perborate solution is added in excess to a chrome alum solution, a greenish-yellow precipitate is produced; when the mixture is shaken with the addition of ether and dilute sulphuric acid, the ether is coloured blue. Percarbonates and hydrogen peroxide do not give this reaction. *Iodates and periodates.*—When a solution containing these salts is treated with chloroform and titanium trichloride solution, a white precipitate forms and iodine is liberated, giving a violet solution in the chloroform; chlorates and perchlorates also liberate iodine from an iodide in the presence of titanium trichloride, but a white precipitate is not formed. Periodates can be distinguished from iodates by the silver nitrate reaction, and also by means of an alcoholic benzidine solution, with which the periodate gives a brown coloration. *Chlorates and perchlorates.*—A portion of the solution is treated with potassium bromide, chloroform, and titanium trichloride solution; bromine is liberated in this test by chlorates, but not by perchlorates. The latter, when treated with methylene-blue solution, yield a violet-coloured precipitate which detonates when heated on a platinum foil. To detect chlorates and perchlorates in the presence of iodates and periodates, the last two must be removed by means of silver nitrate, and the excess of silver by potassium bromide, before the tests are applied. Bromates may be detected in the presence of chlorates and iodates by treating the solution with manganous sulphate solution acidified with sulphuric acid; a violet coloration (manganic sulphate) is produced by bromates, but not by chlorates or iodates. *Persulphates.*—In the absence of iodides and perchlorates, persulphates yield a red precipitate with methylene-blue solution. To identify a persulphate in the presence of a perchlorate, an alcoholic benzidine solution is poured on the surface of the solution under examination; a blue precipitate appears at the junction of the two liquids if a persulphate is present.

W. P. S.

Estimation of Fluorine in Soluble Fluorides. J. G. Dinwiddie (*Amer. J. Sci.*, 1916, [iv], **42**, 464—468).—A neutral solution of the fluoride is heated to boiling and powdered calcium sulphate is added; after one hour, the precipitate, consisting of calcium fluoride and calcium sulphate, is collected on a filter (a disk of filter-paper fitted into a perforated platinum crucible), washed with water saturated previously with calcium fluoride and calcium sulphate, and then washed into an ordinary platinum crucible. The water is evaporated, the disk of filter-paper is ignited, and the ash added to the crucible, and the contents of the latter are then heated at 300° for one hour and weighed. The residue is now sulphated, again heated at 300°, and re-weighed. The difference between the two weights is due to the replacement of 2 atoms of fluorine by the sulphuric acid radicle, and the

quantity of fluorine is found by calculation. The error of the method is about 0·1%. W. P. S.

Estimation of Dissolved Oxygen by Winkler's Method. G. BRUHNS (*Chem. Zeit.*, 1916, **40**, 985—987, 1011—1013. Compare A., 1916, ii, 49).—The alkali solution used in this method should consist of 1 part by weight of potassium hydroxide, 1 part of sodium hydroxide, and 4 parts of water. A stable thiosulphate solution for the final titration is obtained by adding a quantity of alkali sufficient to make the solution distinctly alkaline towards phenolphthalein. After the manganous sulphate has been added to the water and the precipitate allowed to settle, the greater part of the clear supernatant solution may be drawn off before the potassium iodide and hydrochloric acid are added; owing to the lower dilution thus produced, the results obtained are slightly higher than those found by the usual procedure. When potassium hydrogen carbonate is added to convert the manganous hydroxide into carbonate, the small bubbles of air which appear have no effect on the precipitate. W. P. S.

Estimation of Sulphur in Iron and Steel. H. B. PULSIFER (*J. Ind. Eng. Chem.*, 1916, **8**, 1115—1123).—A bibliography covering 285 original articles relating to the estimation of sulphur in iron, etc., is given, and the methods are classified and briefly discussed. Preference is given to the nitro-hydrochloric acid, the chloric acid, and Bamber's methods. Attention is directed to the influence of sulphur segregation and to the importance of obtaining a representative sample for the analysis. W. P. S.

Folin and Denis's Method for the Estimation of Nitrogen by Direct Nesslerisation, and its Application to Spinal Fluids. R. L. KAHN (*J. Biol. Chem.*, 1916, **28**, 203—209. Compare Folin and Denis, A., 1916, ii, 573).—The author finds that the turbidity sometimes produced in the final liquids for colorimetric comparison by this method may be avoided by filtering before the addition of the Nessler's solution instead of after, as described in the original communication (*loc. cit.*). H. W. B.

Comparison of Methods for Estimating Nitrogen in Soils. W. L. LATSHAW (*J. Ind. Eng. Chem.*, 1916, **8**, 1127).—The Gunning method, with the addition of a small quantity of copper wire during the digestion, yielded results which agreed with those found by the Kjeldahl method, and had the advantage that there was no "bumping" during the subsequent distillation of the ammonia. W. P. S.

Estimate of Phosphoric Acid after Citrate Digestion. O. C. SMITH (*J. Ind. Eng. Chem.*, 1916, **8**, 1127—1128).—Two grams of the soil are washed on a filter with about 250 c.c. of water, the filter-paper and its contents are then transferred to a flask containing 100 c.c. of neutral ammonium citrate solution, the

mixture is heated at 60° for thirty minutes, then filtered, and the insoluble portion washed with water at 60° until free from citrate and soluble phosphates. The filter is now placed in a flask and heated with 10 c.c. of concentrated sulphuric acid and 50 c.c. of dilute nitric acid (1:1) until the nitric acid has been expelled; 2 c.c. of concentrated nitric acid are then added, and the heating continued until sulphuric acid fumes appear, at which point a further quantity of nitric acid is added, and the heating again continued. The treatment is repeated until the solution is colourless, and the phosphoric acid is then estimated in the usual way. A clear solution is usually obtained within one hour by this method of oxidising the filter-papers, etc. W. P. S.

The Acidimetric Estimation of Orthophosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 143—146).—Phosphoric acid usually contains an appreciable quantity of carbon dioxide, from which it is freed in the control experiments by heating for several hours in a gold vessel in a stream of purified air. It is then diluted with water free from carbon dioxide. Wagenaar's method (A., 1911, ii, 931) gives satisfactory results if the lead nitrate is added at the Na_2HPO_4 stage, but not otherwise. In Glaser's method, the third hydrogen ion is titrated by adding calcium, strontium, or barium chloride after the solution has become neutral to phenolphthalein, and again titrating until a permanent red coloration is obtained. This only gives accurate results in the presence of an excess of strontium chloride.

The following method is recommended. The dilute solution is first titrated until the red shade of methyl-orange disappears. The second ion is titrated until phenolphthalein becomes a clear red. The solution is then diluted with water free from carbon dioxide, and a neutral solution of silver nitrate is added. The titration is continued with lacmoid as an indicator. C. H. D.

Estimation of Arsenic in Organic Compounds. Arthur James Ewins (T., 1916, **109**, 1355—1358).—The substance is decomposed by means of concentrated sulphuric acid, as in the Kjeldahl process, and the arsenious acid is estimated iodometrically. Trustworthy results are obtained with all but very volatile compounds, and the working details and a number of examples are quoted in the original. J. C. W.

Estimation of Arsenic in Beer and in Dextrose. C. F. Muttelet (*Ann. Falsif.*, 1916, **9**, 326—330).—The Marsh apparatus is recommended for the estimation of arsenic in beer after the organic substances in the latter have been destroyed by treatment with nitric acid, potassium permanganate, and sulphuric acid. An approximate and rapid estimation of the arsenic may be made by treating a portion of the oxidised beer with Bougault's reagent. For the estimation of arsenic in commercial dextrose, a portion of the sample is dissolved in water and then oxidised, as in the case of beer, the resulting solution being tested in a Marsh apparatus.

Samples of dextrose intended for brewing purposes were examined, and many were found to contain from 100 to 400 mg. of arsenic per kilogram. A maximum limit of 4 mg. per kilogram has been fixed, in France, for the quantity of arsenic allowed in dextrose.

W. P. S.

A Boiling Method for the Estimation of Water-soluble Arsenic in Lead Arsenate. GEORGE P. GRAY and A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1916, **8**, 1109—1113).—A quantity of 0·5 gram of the lead arsenate is boiled for ten minutes with 200 c.c. of water, the solution filtered, and the insoluble portion washed with hot water. The filtrate is treated with 1 gram of potassium iodide and 4 c.c. of concentrated sulphuric acid, evaporated to about 40 c.c., then diluted to 200 c.c., and any coloration due to the presence of free iodine is discharged by the addition of $N/20$-thiosulphate solution. The mixture is then nearly neutralised by the addition of concentrated sodium hydroxide solution, using methyl-orange as indicator, an excess of sodium hydrogen carbonate is added, and the arsenious acid titrated with $N/20$-iodine solution. The lead arsenate is not hydrolysed or dissolved during the boiling with water, and the method is trustworthy.

W. P. S.

Apparatus for the Extraction of Sulphur from Arsenic Trisulphide Precipitates. KARL NEUMANN R. VON SPALLART (*Chem. Zeit.*, 1916, **40**, 981).—The Gooch crucible containing the precipitate is supported on a triangle placed in a beaker containing a small quantity of carbon disulphide. A funnel, having a short stem which has been fused up, is fitted into the top of the beaker, and is filled with water. When the carbon disulphide in the beaker is heated, the vapour condenses on the outside of the funnel, and the liquid falls into the crucible, where it dissolves any free sulphur contained in the precipitate.

W. P. S.

Estimation of Boron in Boron-Steel. C. ASCHMAN, jun. (*Chem. Zeit.*, 1916, **40**, 960—961).—The boron is separated by distillation with methyl alcohol, the distillate is evaporated in the presence of ammonium phosphate, and the residue is ignited until all excess of phosphoric acid has been expelled and only boron phosphate remains. About 3 grams of the steel are dissolved in dilute sulphuric acid contained in a flask attached to a condenser; a large excess of acid should be avoided. The ferrous sulphate solution is then oxidised by the addition of hydrogen peroxide, and the mixture is distilled nearly to dryness, the distillate being collected in a receiver containing 20 c.c. of water, 0·5 gram of ammonium carbonate, and a few drops of ammonia; this receiver is connected with a second, containing a small quantity of water. Ten c.c. of absolute, acetone-free methyl alcohol are then added to the contents of the distillation flask, and the distillation is continued. The addition of methyl alcohol, followed by distillation, is repeated five times, and a slow current of air is drawn through

the apparatus for a few minutes between each distillation. Finally, air is drawn through the apparatus for thirty minutes, the contents of the receivers are then transferred to a weighed platinum basin containing 1 gram of ammonium phosphate, the mixture is evaporated to a syrupy consistence, and then heated at 1000° in an electric furnace until the residue of boron phosphate (BPO_4) is constant in weight. W. P. S.

The Oxidation of Coal. GEORGES CHARPY and MARCEL GODCHOT (*Compt. rend.*, 1916, **163**, 745—747).—When coal is heated at 100° for three hours, it loses in weight an amount equal to the loss in weight on drying the coal in a vacuum at the ordinary temperature, which is the moisture content of the coal. If the heating is continued for three months, there is an increase in weight, due to oxidation, equal to 3—5% of the original weight of the coal, there being at the same time a diminution of 3—13% in the calorific power. The content in ash and volatile substances is not appreciably modified by this prolonged oxidation. It is necessary therefore to make a direct determination of the calorific power of a coal to ascertain its value as a fuel. W. G.

[Estimation of the] Total Carbon in Soil by Wet Combustion. C. J. SCHOLLENBERGER (*J. Ind. Eng. Chem.*, 1916, **8**, 1126).—Slight modifications of a method proposed by Ames and Gaither (A., 1914, ii, 676) are recommended. A mixture of sulphuric and phosphoric acids with chromic acid is used for the oxidation, and the carbon dioxide formed is absorbed in barium hydroxide solution. The barium carbonate is titrated as described by Cain (A., 1914, ii, 577), or the excess of barium hydroxide is titrated according to Truog's method (A., 1916, ii, 113).
W. P. S.

Apparatus for the Estimation of Rare Gases (Argon). AD. SIEVERTS and RICH. BRANDT (*Zeitsch. angew. Chem.*, 1916, **29**, 402—406).—An apparatus for the estimation of argon by means of metallic calcium is described, the method depending on the fact that calcium at 450° to 550° absorbs nitrogen and all other gases with the exception of those belonging to the argon group. The apparatus consists of a tube containing the metallic calcium and attached to a manometer; three-way taps are provided at the top of the two arms of the manometer, and connect with tubes for exhausting the apparatus, for admitting the gas, and for admitting air to one of the arms. About 5 grams of calcium are placed in the tube, the latter is placed horizontally in a small oven, heated at 450° to 550°, and the air is exhausted from the apparatus; the tube is then cooled, turned to a vertical position, and placed in a vessel containing cold water. The gas under examination is now admitted, the pressure noted, the calcium tube is again heated as before, and when the pressure no longer decreases (the absorption requires about one hour), the tube is cooled and the pressure again noted. If P was the original pressure and p the final pressure,

the gas under examination contains $100p/P\%$ of rare gases by volume. If the gas contains a large proportion of carbon monoxide, carbon dioxide, methane, etc., it should be subjected to a preliminary purification, but when only air is present in addition to rare gases, the mixture may be treated directly. W. P. S.

Oxidimetric Estimation of Cuprous Oxide Precipitated during the Analysis of Sugar with Fehling's Solution. J. ROLLE (*Chem. Zentr.*, 1916, ii, 693—694; from *Zeitsch. Spiritus-industrie*, 1916, **39**, 272).—The process depends on the reaction

$$Cu_2O + Fe_2(SO_4)_3(NH_4)_2SO_4 + H_2SO_4 = 2CuSO_4 + FeSO_4(NH_4)_2SO_4 + FeSO_4 + H_2O.$$

The requisite solutions are obtained (1) by dissolving potassium permanganate (5 grams) in water and making the solution up to 1 litre, the solution being standardised after a few days, and (2) by dissolving ferric ammonium alum (80 grams) in water (800 c.c.), filtration through glass wool, addition of concentrated sulphuric acid (50 c.c.), and of water sufficient to bring the volume of the solution to 1000 c.c. The sugar solution is treated in the usual manner with Fehling's solution, and the clear liquor decanted through an Allihn filter tube; the precipitated cuprous oxide is washed with hot water, allowed to subside, and the liquid again filtered. The cuprous oxide is now dissolved by first slowly drawing 50 c.c. of ferric ammonium alum solution through the filter, and then adding the filtrate to the main bulk of the cuprous oxide and heating to boiling, when the cuprous oxide dissolves completely. Potassium permanganate is then added to the boiling, bluish-green solution until a permanent brownish-green coloration is obtained. H. W.

Oxalate–Iodide Process for Paris Green Analysis. C. A. PETERS and L. E. FIELDING (*J. Ind. Eng. Chem.*, 1916, **8**, 1114—1115).—A method which yields trustworthy results consists in precipitating the copper as oxalate and titrating the oxalate with permanganate; the filtrate from the copper oxalate precipitate is treated with an excess of sodium hydrogen carbonate, and the arsenic then titrated with iodine solution. The details of the method are as follows: 0·25 gram of the sample is boiled with 50 c.c. of water and 1 c.c. of dilute sulphuric acid (1:10) until dissolved, 2 grams of solid oxalic acid are added to the hot solution, and, after eighteen hours, the copper oxalate is collected on an asbestos filter and washed. The filter and precipitate are then transferred to a beaker, heated with 10 c.c. of sulphuric acid (1:1), and the solution is titrated with standardised permanganate solution. W. P. S.

Estimation of Chromium in Ferrochrome. WILH. HERWIG (*Chem. Zentr.*, 1916, ii, 693; from *Stahl u. Eisen*, 1916, **36**, 646—650).—The volumetric estimation of chromium in ferrochrome by means of potassium permanganate gives low results if the theoretical titer number for chromium as recorded in the textbooks (0·310 instead of the empirical number 0·3165) is used. On

the other hand, accurate results are obtained by the sodium thiosulphate and potassium dichromate methods. The following shortened sodium thiosulphate process gives results accurate to 0·3%, and can be completed in an hour. The specimen is passed through a sieve of 2700 meshes to the sq. cm.; 0·5 gram of the product so prepared is fused in an iron crucible with sodium peroxide (5—6 grams), gentle heating being used for about a minute until the metal has dissolved in the fused mass, after which it is heated, with gentle agitation, for two minutes with the full Bunsen burner. The somewhat cooled crucible is transferred to a beaker containing about 350 c.c. of water at 60—80°, the beaker immediately covered with a clock-glass, and the water cautiously boiled for five minutes to decompose the sodium peroxide completely; after being cooled, the solution is diluted to 500 c.c. and passed through a double filter. One minute after dilution of 100 c.c. of the filtrate to about 300 c.c. with water, and addition of potassium iodide (1 gram) and hydrochloric acid (D 1·124, 40 c.c.), the titration is effected with sodium thiosulphate.

Decomposition of ferrochrome by magnesium carbonate mixture is frequently incomplete. After being sieved, the specimen should be ground for two to three hours in an agate mortar, and the mixture must be heated for at least an hour with a powerful blowpipe flame. The residue from the first operation must be once more, at least, similarly treated. H. W.

The Physical Character of Precipitated Lead Molybdate and its Importance in the Estimation of Molybdenum and Lead. HARRY B. WEISER (*J. Physical Chem.*, 1916, **20**, 640—662).—The precipitation of lead molybdate has been examined with a view to its employment in the estimation of lead and molybdenum.

The precipitate obtained by mixing solutions of ammonium heptamolybdate and lead acetate, or the lead salt of any weak acid, is bluish-white in colour, flocculent, and bulky, and in this form it is unsuitable for quantitative work. A precipitate of similar character is obtained when solutions of sodium molybdate and any soluble lead salt are mixed. On the other hand, the precipitate obtained from solutions of ammonium heptamolybdate and the lead salt of any strong acid is more granular and much less bulky, and has a yellowish-white colour. A similar precipitate is thrown down with all lead salts if a little nitric acid or an excess of sodium or ammonium acetate is added to the solution of sodium or ammonium molybdate before precipitating. Since freshly precipitated lead molybdate is freely soluble in nitric and other strong acids and slightly so in sodium and ammonium acetate solutions, the above-described results can be readily explained in terms of this solvent action.

Lead molybdate tends to absorb ammonium molybdate from solution, and this effect is sufficiently pronounced in the case of the flocculent modification to cause a darkening of the precipitated salt when this is gently ignited. This is due to the decomposition

of the ammonium molybdate, which forms a blue oxide when heated at about 200°.

In presence of an excess of ammonium molybdate, the lead salt yields a colloidal solution, from which, however, the lead molybdate is precipitated in presence of a little nitric acid. The coagulation of the negative colloid is attributed to the neutralisation of the negative charge by the adsorption of hydrogen ions.

The above results indicate the conditions which are required for quantitative precipitation of lead molybdate, and detailed instructions are given for the application of the method in the estimation of both lead and molybdenum. H. M. D.

Electroanalysis of Tin without Platinum Electrodes. T. Batuecas (*Anal. Fis. Quim.*, 1916, **14**, 495—511).—An application of Guzmán's method with a copper cathode and a graphite anode to the estimation of stannous and stannic tin in salts and of the metal in alloys. Hydrochloric acid is employed as electrolyte in the estimation of the salts, a mixture of this acid with tartaric acid in the separation of tin from zinc and from cadmium, and an ammoniacal tartrate solution in the separation of tin from silver. A. J. W.

Microanalysis of Wine. Maximilian Ripper and Franz Wohack (*Chem. Zentr.*, 1916, ii, 696—697; from *Zeitsch. landw. Versuchs-Wesen. Österr.*, 1916, **19**, 372—381).—Wohack's method of estimating glycerol in wine (A., 1915, ii, 589) is critically discussed, and has been modified to render it suitable for microanalysis. 0·5 C.c. of wine which has been evaporated to half its original volume and treated with barium acetate and tannin (100 c.c. of wine, 10 c.c. of barium acetate solution [10%], and as much tannin as can be placed on the point of a knife) is brought into the decomposition flask and treated with 1·5 c.c. of hydriodic acid (D 1·96). The decomposition vessel is a quartz or glass tube filled with platinised quartz or platinised asbestos, and is shielded from direct contact with the flame by asbestos paper and iron gauze. The rest of the process is the same as that previously described. The complete process, including evaporation of the wine, occupies one and a-half hours, and gives very accurate results with a minimum expenditure of time, labour, and cost. H. W.

Estimation of Sugar in Blood. Charles G. L. Wolf and Walter C. Ball (*J. Roy. Army Med. Corps*, 1916, **27**, 691—703).—Criticism of Bang's micro-method (compare A., 1907, ii, 136; 1908, ii, 235, 739). Various modifications have been tried, and the following, using titanium trichloride, has been adopted (compare Knecht and Hibbert, A., 1903, ii, 509, and "New Reduction Methods in Volumetric Analysis," pp. 46—47).

The blood (0·1—0·2 gram) is absorbed and weighed in a brush of glass wool and aluminium wire, and is washed out twice with 5 c.c. of 22% potassium chloride in $N/125$-hydrochloric acid. The

solution is filtered from glass fibres through asbestos or through a quantitative filter-paper, and the filtrate is heated with a few c.c. of a diluted Fehling's solution (10 c.c. of each of the ordinary pair of solutions are mixed and diluted to 100 c.c.). The heating takes place in a 60 c.c. flask provided with a stout rubber tubing over the mouth, first over a naked flame to incipient ebullition (25 secs.), and then on a sand-bath (gentle boiling for two and a-half minutes). The rubber mouthpiece is then clipped with forceps, and the flask is cooled. About 4 c.c. of *N*-hydrochloric acid and an accurately measured volume (1·5—2 c.c.) of titanium trichloride solution are added. (The latter is prepared by boiling 50 c.c. of the commercial 20% solution for one minute with 100 c.c. of concentrated hydrochloric acid, and making up to 2 litres; it is stored as described in Knecht and Hibbert's book.) Subsequently, 4 c.c. of 50% ammonium thiocyanate are added as indicator, and the solution in the flask is titrated with a ferric solution containing 1/400 gram atom per litre (prepared by oxidising 0·9805 gram of ferrous ammonium sulphate by boiling in slightly alkaline solution with a slight excess of hydrogen peroxide for ten minutes, adding 20 c.c. of concentrated hydrochloric acid, and making up to 1 litre). One c.c. of this ferric solution = 0·107 mg. dextrose.

The estimation is thus indirect and based on the determination of the unreduced copper, which is reduced by titanium trichloride, and the excess of the latter is titrated with the ferric solution. Nevertheless, the method is advantageous in having a sharper and more permanent end-point than that of Bang's iodometric one.

G. B.

Gravimetric Estimation of β-Hydroxybutyric Acid. DONALD D. VAN SLYKE (*Proc. Soc. Exp. Med., New York*, 1916, **13**, 134; from *Physiol. Abstr.*, 1916, **1**, 197).—If β-hydroxybutyric acid is oxidised with potassium dichromate in the presence of sulphuric acid and mercuric sulphate, a precipitate of the acetone compound of mercuric sulphate can be obtained in an amount proportional to the acid present. If 175 c.c. of a β-hydroxybutyric acid solution containing 9% of sulphuric acid, 2% of mercuric sulphate, and 0·25 gram of potassium dichromate are boiled under a reflux condenser for one hour, 7·7 mg. of the mercury–acetone compound are precipitated for each mg. of acid present. The acid may vary from 1 to 9 mg. without affecting the ratio if the concentrations of the other reagents are kept constant. G. B.

Modified Benedict and Hitchcock Uric Acid Standard Solution. L. J. CURTMAN and M. FREED (*J. Biol. Chem.*, 1916, **28**, 89—92).—The substitution of boric acid for acetic acid in the preparation of the standard uric acid solution (compare Benedict and Hitchcock, A., 1915, ii, 602) is advisable in cold weather, because the uric acid does not then crystallise out so readily. In warm weather, however, the modified standard deteriorates more rapidly than the original acetic acid standard. H. W. B.

Systematic Detection of Thiocyanates. LOUIS J. CURTMAN and BEN R. HARRIS (*J. Amer. Chem. Soc.*, 1916, **38**, 2622—2629).—The sensitiveness of the reaction between thiocyanate and ferric chloride has been investigated, alone and in the presence of iodide, acetate, and nitrite. It is shown that 0·1 mg. of thiocyanate may be detected by means of ferric chloride. It is also shown that 7 mg. of iodide, 18 mg. of acetate, and 14 mg. of nitrite yield the same colour with ferric chloride as does 0·1 mg. of thiocyanate. These quantities therefore represent the limiting amounts which may be present in mixtures in which thiocyanate is to be detected. For the detection of thiocyanates, the authors recommend the following procedure. The solution is rendered just alkaline with sodium hydroxide, and excess of barium nitrate, calcium nitrate, and cobalt nitrate is added, and 3 grams of washed asbestos fibre. The mixture is boiled for half a minute, with vigorous stirring, filtered on a fluted paper, and washed until the filtrate is only faintly pink. The filtrate is acidified with five drops of 10% nitric acid, and excess of silver nitrate added. The mixture is boiled for a minute, filtered, and washed until the washings are no longer pink. The filter-paper and contents, containing the chloride, iodide, and thiocyanate, is treated with 10 c.c. of 5% sodium chloride solution, and the mixture kept at the boiling point for five minutes and filtered. The filtrate is concentrated to 4 c.c., treated with a drop of nitric acid (10%), and 0·5 c.c. of $2N$-ferric nitrate solution. The presence of thiocyanate is indicated by the usual blood-red coloration. An approximately quantitative method for estimating thiocyanates is based on the discharge of the blood-red colour by a solution of mercuric chloride. It is shown that the reaction is better if the ferric thiocyanate solution is titrated with mercuric chloride until a definite standard brown tint is produced, and not until complete discharge of the colour has been obtained. A large number of tests are quoted to show the trustworthiness of the test under different conditions. J. F. S.

Halogenation. XIII. Methods of Estimation of Semicarbazide, Semioxamazide, and Oxalylhydrazide by their Interactions with Halogens and Halogen Oxyacids. RASIK LAL DATTA and JOGENDRA KUMAR CHOUDHURY (*J. Amer. Chem. Soc.*, 1916, **38**, 2736—2739. Compare A., 1914, ii, 504).—The authors now note that if a solution of semicarbazide chlorate is allowed to evaporate in a vacuum desiccator, instead of being decomposed on a water-bath, the chlorate is formed, and as soon as it assumes the solid state, it explodes violently. Attempts were made to isolate semicarbazide nitrite by the interaction of semicarbazide hydrochloride and silver nitrite, but the only product was carbamide.

Semioxamazide is decomposed in the same way as semicarbazide by the action of potassium bromate, iodate, or periodate in the presence of dilute sulphuric acid, three-fourths of its total nitrogen being liberated. With bromine water or sodium hypobromite, the whole of the nitrogen is liberated. Oxalylhydrazide is also decom-

posed by all these reagents, the whole of its nitrogen being liberated in every case. $C_2O_2(NH\cdot NH_2)_2 + 2O_2 = CO + CO_2 + 3H_2O + 2N_2$.

Potassium chlorate and dilute sulphuric acid do not cause any of the above oxidations. W. G.

Estimation of Theobromine and Caffeine in Cacao and Chocolate. G. SAVINI (*Ann. Chim. Applicata*, 1916, **6**, 247—250).—The following method, tested on artificial mixtures and on natural products, is found to give satisfactory results.

Twelve grams of the powdered cacao or chocolate are boiled with 70 c.c. of light petroleum on a water-bath in a flask of about 500 c.c. capacity for ten minutes, the hot solvent being decanted on to a small filter, and the operation repeated twice with fresh quantities of light petroleum. The solvent is removed by heating the flask containing the defatted substance, and also the funnel, in an oven for a few minutes. The filter-paper is then placed in the flask, together with 5 c.c. of 10% sulphuric acid and about 250 c.c. of water, and the whole boiled under a reflux condenser for an hour. The hot liquid is introduced into a 300 c.c. measuring flask, together with the hot water used for rinsing out the flask, the filter-paper being prevented from entering. The solution is not cooled to lower than about 30°, and is then made up to volume and filtered. Of the filtrate, 250 c.c., corresponding with 10 grams of the original material, are evaporated to a syrup in a porcelain dish with 10 grams of fine sand and sufficient magnesia to render it distinctly alkaline. The syrup is mixed with a further quantity (8—10 grams) of magnesia so as to give a dry, pulverulent substance, which is scraped off with a spatula and powdered. The powder is treated in a flask with 100 c.c. of chloroform, the pestle, spatula, and dish being washed twice with 5 c.c. of hot water, and the latter added to the chloroform, which is boiled with 0·25 c.c. of concentrated ammonia solution for fifteen minutes in a reflux apparatus. The boiling chloroform is filtered through a pleated filter-paper, and the residue in the flask boiled again with four separate quantities of 100 c.c. each of chloroform. The whole of the filtered chloroform is distilled off on a water-bath, the last traces of the solvent being removed by drying the flask in an oven. The residue is washed with two successive quantities of 10 c.c. of light petroleum, which is decanted on to a small filter, and is then dissolved in a little boiling water, which is filtered through the same filter into a tared platinum or glass dish. The flask is rinsed out three times with small quantities of boiling water, and the whole evaporated on a water-bath, the residue being dried for an hour in an oven at 100° and weighed. The weight of the dry residue, multiplied by ten, gives the percentage of alkaloids (theobromine and caffeine) in the original material. The alkaloids thus extracted are almost colourless and of sufficient purity, the proportion of mineral matter in them being inappreciable. T. H. P.

A Biological Method for the Estimation of Choline. HERMANN FÜHNER (*Biochem. Zeitsch.*, 1916, **77**, 408—414).—The

isolated heart of a frog is a better subject for the biological estimation of choline (in the form of its acetyl derivative) than is the loop of intestine of a guinea-pig, which has hitherto been chiefly used for this purpose. As many as twenty experiments can be carried out in a day by this method. Acetylcholine is about 100,000 times more active as regards the frog's heart than is choline itself. The paper is illustrated by several chymographic records illustrating the action of acetylcholine. S. B. S.

A Hitherto Neglected Factor affecting the Estimation of Minute Quantities of Creatinine. ANDREW HUNTER and W. R. CAMPBELL (*J. Biol. Chem.*, 1916, **28**, 335—348).—McCrudden and Sargent (A., 1916, ii, 587) have recently directed attention to the untrustworthiness of creatinine estimations by Folin's method, because of the development of a red colour by the interaction of picric acid and sodium hydroxide in the absence of any creatinine. The present authors find that this occurs only when the picric acid solution has been kept for a considerable time, and is due to the production of a chromogenic substance from the picric acid by the action of light, with possibly other agencies. When the picric acid solutions are preserved in the dark, they may safely be employed for creatinine estimations within a period of at least two months; otherwise, picric acid solutions more than a month old should not be employed. When this precaution is attended to, the Folin method is found to possess a high degree of accuracy.

The authors have also prepared curves showing the actual relation of colour intensity to creatinine concentrations which enables the colour comparisons to be made over a wider range than is generally considered permissible. H. W. B.

Detection of Albumin in Urine. EICKE (*Chem. Zentr.*, 1916, ii, 697; from *Deut. med. Woch.*, 1916, **42**, 1039).—Pandy's reaction has been recommended by Liebers (A., 1916, ii, 594) for the detection of albumin in urine. The author finds, however, that the method is not sufficiently sensitive for this purpose. The limit at which a distinct reaction is obtained lies at 0·2%. Lack of sensitiveness is attributed to the fact that phenol only indicates the presence of globulins, and does not react with serum-albumin. H. W.

A Test for Albumin for Use by the Military Surgeon. ADOLF EDELMANN (*Chem. Zentr.*, 1916, ii, 524; from *Wien. Klin. Woch.*, 1916, **29**, 901).—Resorcinol is a suitable reagent for the detection of albumin during campaign.

A small quantity of resorcinol is dissolved in the minimum amount of spring water, and the solution is covered with a few c.c. of urine; a white ring at the junction of the layers shows the presence of albumin. If the urine is added drop by drop to the resorcinol solution, the presence of albumin is indicated by an intense turbidity. The test is more sensitive than the potassium

ferrocyanide or sulphosalicylic acid reactions, and is not vitiated by the presence of any normal or pathological constituent of urine.
H. W.

Certain Methods for the Study of Proteolytic Action. H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1916, **38**, 2199—2216. Compare Long and Barton, A., 1914, ii, 827; Harding and MacLean, A., 1916, ii, 459).—A comparative examination of some eight different methods for the measurement of proteolytic action. The methods tested were: (1) the Mett method (compare Cobb, A., 1905, ii, 466); (2) estimation of total nitrogen in the digestion products; (3) measurement of increase of amino-nitrogen by van Slyke's method; (4) titration of the acidity of the digestion products; (5) the increase of electrical conductivity; (6) the polariscopic method; (7) colorimetric measurements in the biuret reaction; and (8) in the ninhydrin reaction. The enzymes used were commercial samples of pepsin and trypsin, and the proteins of egg-albumin or casein.

In general, methods (2) or (3) or both appear to be more delicate as a means of detecting proteolysis than either methods (7) or (8), and more delicate, accurate, and generally applicable as a means of measurement than any of the other methods studied.

It is essential in quantitative comparisons so to limit the amount of enzyme preparation used and the time of action as to keep within the region in which the velocity of hydrolysis is directly proportional to the enzyme concentration. The most suitable time is half an hour to one hour.
W. G.

Influence of Carbohydrates on the Accuracy of the Van Slyke Method in the Hydrolysis of Caseinogen. E. B. HART and BARNETT SURE (*J. Biol. Chem.*, 1916, **28**, 241—249).—The Van Slyke method (A., 1911, ii, 944) for the estimation of certain amino-acids or groups of amino-acids in protein was employed by him for the analysis of pure proteins. Later workers have applied the same method directly to such materials as cattle foods containing carbohydrates and fats, as well as proteins. The authors now show that when the method is applied to a mixture of caseinogen and various carbohydrates, the amounts of the different amino-acids obtained vary according to the particular carbohydrates contained in the mixtures. This variation is specially apparent in the hexone bases and non-amino-nitrogen. The direct application of the Van Slyke method to cattle foods affords therefore inaccurate results (compare Roxas, A., 1916, i, 797).
H. W. B.

The Alcohol Test for Milk. I. M. KOLTHOFF (*Pharm. Weekblad*, 1916, **53**, 1589—1599).—The author finds that the action of the alcohol test for milk is dependent on the presence of calcium ions, and that the method is of hygienic and pathological-chemical importance.
A. J. W.

Technique of the Diazo- and Urochromogen-reactions. ZUCKER and RUGE (*Chem. Zentr.*, 1916, ii, 352—353; from *Münch. Med. Woch.*, 1916, **63**, 918).—The following method of performing the Ehrlich diazo-reaction is recommended: 10 c.c. of solution I [sulphanilic acid (5 grams) and hydrochloric acid (D 1·19, 50 grams) in water (1000 c.c.)] are mixed with four drops of solution II [sodium nitrate (0·5 gram) in water (100 c.c.)], 10 c.c. of urine are added, and 3 c.c. of 25% ammonia; if the froth becomes pink on shaking, a positive reaction is indicated. For the urochromogen reaction, the clear urine (10 c.c.) is diluted until colourless, and the dilute urine placed in two similar test-tubes. Five drops of potassium permanganate solution (1:1000) are added to one tube with stirring, and, after half a minute, the colours of the two tubes are compared by daylight. A distinct, canary-yellow coloration of the urine treated with permanganate shows a positive reaction; a pink coloration shows that the urine is too greatly diluted. If the coloration is at first yellow, but disappears after a minute, the reaction is negative; in cases of positive reaction, the intensity of the yellow coloration increases. H. W.

The Absorption of Organic Dyes by Colloidal Soils, Clays, etc. WILHELM GRAF ZU LEININGEN (*Kolloid Zeitsch.*, 1916, **19**, 165—172).—Comparative experiments with various dyes have shown that methylene-blue is the most suitable for use in the investigation of different soils. The assumption that dyes are rapidly absorbed is not in agreement with the author's experience, according to which the process is not complete until after the lapse of several months.

The application of dye absorption in the analysis of soils is critically discussed in reference to the results of experiments, which show that the absorption bears no simple relation to the colloid substances present in the soil. H. M. D.

General and Physical Chemistry.

Spectrographic Studies of some Portuguese Uranium and Zirconium Minerals. A. Pereira-Forjaz (*Compt. rend.*, 1917, **164**, 102—103).—From the spectrographic examinations of specimens of chalcolite from Sabugal and Nellas, autunite from Nellas, and of zircon from the syenite with riebeckite from Alter Pedroso, the elements present in these minerals are given. It is found that carnotite accompanies autunite and chalcolite in the radio-uraniferous district of Portugal, and other uranium minerals also occur with these two, namely, walpurgite, trögerite, and zeunerite. The radium ray $\lambda = 4682{\cdot}4$ is more sensitive than the more intense ray $\lambda = 3814{\cdot}6$. The zirconium ray $\lambda = 4739{\cdot}5$ does not appear to be very sensitive. W. G.

The Circular Polarisation Produced by the Spherolites with Helicoidal Winding. Paul Gaubert (*Ann. Physique*, 1916, [ix], **6**, 356—364).—A more detailed account of work already published (compare A., 1916, ii, 604). W. G.

Inner Mechanism of the Reaction of the Photochemical Oxidation of Hydrogen Iodide. N. P. Strachov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 824—837).—According to Plotnikov ("Kinetics of Photochemical Reactions," Moscow, 1908), the oxidation of hydrogen iodide in aqueous solution by oxygen under the influence of sunlight proceeds according to the scheme:

$$d(O_2)/dt = kJ(KI)^{2/3}(HCl)^{2/3}(O_2),$$

and if the potassium iodide and hydrogen chloride are taken in excess in relation to the oxygen, the reaction is of the first order. At first glance, the light-sensitive component in this case would appear to be the iodine atom in the hydrogen iodide molecule. With this view, certain peculiarities of the reaction are not in accord, especially its insensitiveness to the free iodine formed, which, as it absorbs the active blue and violet light, should play the part of a light-filter. The theory of the reaction was also developed by Plotnikov ("Investigation of Photochemical Phenomena," II, Moscow, 1915), who, on the assumption that the photochemical component is the colourless iodine ion, which should absorb blue light to an infinitely slight extent, derived the equation $dx/dt = kJ_0ia^{2/3}(b-x)$, where $(a-x)$ and $(b-x)$ are the concentrations of the hydrogen iodide and oxygen respectively, J_0 the intensity of the light impinging on the reacting mixture, i the natural coefficient of absorption for blue light, and k the velocity constant. The iodine formed, giving rise to yellowish-brown compounds, may be expected to retard the reaction, so that the equation becomes modified to $dx/dt = kJ_0e^{-i_2px} \, . \, a^{2/3}(b-x)$, where i_2 is the coefficient of absorption of blue light by the iodine solution formed and p the thickness of the reacting layer.

That iodine does exert such a retarding influence is shown by interposing iodine solution between the source of light and the reacting mixture. When, however, the effect of iodine acting as an "internal" light-filter is investigated, different results are obtained. Between the limits of concentration, 2·7 and 27 millinormal, iodine exhibits no retarding action, although a solution of the latter concentration completely stops the reaction when used as an "external" light-filter. When, however, the concentration of the iodine reaches the value 54 millinormal, a rapid fall occurs in the velocity constant, the rate of fall being gradually diminished with further increase in the concentration of the iodine. The diminution in the value of the velocity constant is therefore not related simply to the concentration of the iodine. It is pointed out that, owing to change in the iodine complexes, iodine solutions do not conform to Beer's Law.

This disagreement between the observed retardation of the reaction and that assumed by Plotnikov is explained by the author on the supposition that one of the iodine complexes formed is a photochemical autocatalyst, and that such complex is only slightly sensitive to light. This supposition leads to an equation of the first order with respect to $(b-x)$, the concentration of the oxygen.

T. H. P.

Thermo-electric Properties of Certain Polymorphous Metals. P. N. LASCHTSCHENKO, S. F. BYKOV, and S. V. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 279—296).—Measurements have been made at different temperatures of the thermo-potentials of a number of pairs of metals, one metal in each case being capable of existing in polymorphous modifications; the numerical results are given, and also the curves showing the connexion between electromotive force and temperature.

The nickel–platinum curve shows a characteristic bend in its early part, but no break, and the temperature-coefficient of the thermoelectric force $(\partial E/\partial t)$ exhibits a minimum at about 400°. With iron–platinum, $\partial E/\partial t$ has minima at 475° and 1025°, and a maximum at 850°, the last temperature corresponding nearly with the transformation of β- into γ-iron (compare Broniewski, A., 1913, ii, 288).

With zinc–platinum, zinc–palladium, zinc–gold, and zinc–iron, the results obtained bear little relation to allotropic change of the zinc. With zinc–copper, however, this change is sharply shown, the neutral point, at which the thermoelectric force is a maximum, being at about 240°; at 310°, the curve again assumes its regular parabolic form, this temperature being regarded as that of the transformation of the zinc. The tin–platinum curve shows no peculiarity, but the tin–nickel curve consists of two branches meeting at a very slight angle at 160—165° (compare Degens, A., 1909, ii, 888; Werner, A., 1913, ii, 1057). The influence of the allotropy of thallium on the thermoelectric properties of the metal appears, from a study of thallium–platinum, thallium–copper, and thallium–nickel, to be only slight (compare Werner, *loc. cit.*).

Investigation has been made of aluminium paired with platinum, palladium, silver, and constantan, the aluminium employed containing 1·30% Si, 0·85% Fe, and traces of copper. In all these cases, the curves exhibit changes in direction at temperatures lying within the limits 570—590°, which are in agreement with those observed by other investigators in other ways. T. H. P.

Electrolytic Dissociation of Individual Salts. A. N. SACHANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 341—361. Compare A., 1915, ii, 729, 730).—The author's previous work on the electrical conductivity of silver nitrate in solution in different solvents indicates that, even in absence of solvent, this salt exhibits electrolytic dissociation, and in the present paper the consequences of this result, and its bearing on the conclusions drawn by various investigators, are discussed.

It may be regarded as an established fact (compare Foussereau, A., 1886, 844, 975; Poincaré, A., 1889, 457; 1890, 551) that the degree of dissociation of fused binary salts depends not at all or but slightly on the temperature, the diminution in conductivity of the fused salts with fall of temperature being the result only of the increased viscosity, and consequent diminished ionic velocity. The conclusion is therefore drawn that if such fused salt were under-cooled to a low temperature, for instance, 25°, its degree of dissociation would be of the same order as with the ordinary fused condition (compare Walden, A., 1914, ii, 330). The inaccuracy of the view that the dissociation of fused salts is due largely to their high temperatures is pointed out (compare Noyes, "The Electrical Conductivity of Aqueous Solutions," Washington, 1907).

With the change from the fused to the solid state, the electrical conductivity of a salt, such as silver nitrate, diminishes enormously, and such diminution may be due to diminution of either the electrolytic dissociation of the salt or the mobility of the ions. In order to decide between these two alternatives, the author makes use of a cell containing two silver electrodes immersed in silver nitrate, of which the portions in contact with the two electrodes may be kept at different temperatures. It is found possible to keep the silver nitrate in contact with one electrode in the fused, and that in contact with the other electrode in the crystalline condition, the temperatures in the two cases being the same; repeated measurements show that, under such conditions, the electromotive force of this cell is zero (compare Negbaur, *Ann. Phys. Chem.*, 1892, [ii], **47**, 27). From this result, the conclusion is drawn that the concentrations of the silver ions in fused and crystalline silver nitrate at the melting point are identical, the sharp fall in the specific conductivity of the fused salt on crystallisation being due to the diminished ionic velocity. It follows, then, that crystalline binary salts (normal electrolytes) are dissociated electrolytically to approximately the same extent as in the fused state, and it may reasonably be assumed that the degree of this dissociation depends but little on the temperature (compare

R. Lorenz, "Elektrolyse geschmolzener Salze," III, 289; Tubandt and E. Lorenz, A., 1914, ii, 516).

It follows, further, that the current view that salts are resolved into ions on solution is invalid, dissolution only changing the degree of dissociation of indivdual salts to an extent depending on the dielectric properties of the solvent and on such change, usually comparatively inconsiderable, in the electro-affinities of the ions as is caused by possible solvation processes. The idea of the dissociating capacities of solvents as the cause of dissociation of salts also appears quite superfluous. Moreover, one of the strongest arguments against the theory of electrolytic dissociation, namely, the absence of any peculiarity attending the dissolution of salts, vanishes entirely.

The above considerations relate solely to normal electrolytes. Such compounds as hydrogen chloride or aluminium chloride, which in the individual state are non-conductors, undergo more profound change on dissolution; indeed, in these cases, the marked thermal effects accompanying dissolution are evidences of reciprocal action between solvent and salt.

If ionic structure determines the chemical properties of substances, it none the less sharply characterises their thermodynamic relations. Compounds possessing such structure are distinguished by marked reactivity in those conditions which thermodynamics represents as possible for different processes. Finally, one of the most important properties of salt-like substances, namely, their ability to form polymerides and complexes, is also a necessary consequence of their polar structure. T. H. P.

Fuel Cells at High Temperatures. EMIL BAUR, AGNES PETERSEN, and G. FÜLLEMANN (*Zeitsch. Elektrochem.*, 1916, **22**, 409—414. Compare A., 1913, ii, 13).—In a previous paper (*loc. cit.*), various fuel cells were described in which the cathode consisted of molten silver which was saturated with oxygen. The present paper describes a series of fuel cells in which the silver cathode is replaced by easily dissociated oxides. The *E.M.F.* of the following combinations has been determined at temperatures ranging from 700° to 1300°: (i) CuO,Cu_2O | electrolyte | C; (ii) PbO,Pb | electrolyte | C; (iii) Fe_3O_4,FeO | electrolyte | CuO,Cu_2O; (iv) FeO,Fe | electrolyte | CuO,Cu_2O;

(v) NiO,Ni | electrolyte | CuO,Cu_2O;

and (vi) PbO,Pb | electrolyte | CuO,Cu_2O. The electrolyte was borax, glass, or porcelain. In the case of the first combination, rather fluctuating values for the *E.M.F.* were found, ranging up to 1·4 volts at 1200°. The lead oxide combination (ii) gave an *E.M.F.* of about 1·0 volt at 1200°. In the third cell, *E.M.F.* values between 0·7 and 0·8 volt were obtained for temperatures between 700° and 960°. The nickel oxide–copper oxide cell gave a value 0·717 volt at 860°, whereas the lead oxide–copper oxide gave a value of 0·44 volt at 990°. The theoretical voltages obtainable from these cells are calculated, and the reasons for any differences discussed. J. F. S.

Oxygen Pressure of some Oxides and the Carbon-Oxygen Cell at High Temperatures. W. D. Treadwell (*Zeitsch. Elektrochem.*, 1916, **22**, 414—421. Compare preceding abstract).—The oxygen pressure of the oxides of copper, lead, nickel, and iron has been deduced from measurements of the potential of these oxides measured against an electrode of molten silver saturated with oxygen. The measurements were carried out at temperatures from 800° to 1193° with electrolytes consisting of molten borax or easily fusible glass mixed with quartz or porcelain. The cells measured were: (i) $Cu_2O,CuO|$electrolyte$|O_2,Ag$; (ii) $Fe_3O_4,Fe_2O_3|$electrolyte$|O_2,Ag$; (iii) $Cu,Cu_2O|$electrolyte$|O_2,Ag$; (iv) $Pb,PbO|$electrolyte$|O_2,Ag$; (v) $Ni,NiO|$electrolyte$|O_2,Ag$; (vi) $FeO,Fe_2O_3|$electrolyte$|O_2,Ag$; (vii) $Fe,FeO|$electrolyte$|O_2,Ag$; and (viii) $C|$electrolyte$|O_2,Ag$. At 1000°, the observed potential was: (i) 0·045 volt, which gives a value of Q for the change $Cu_2O+\frac{1}{2}O_2=2CuO$ of 31,200 cal.; (ii) 0·262 volt, giving the Q value 49,500 cal. for the change $2Fe_3O_4+\frac{1}{2}O_2=3Fe_2O_3$; (iii) 0·367 volt, $Q=40,200$ cal. for $2Cu+\frac{1}{2}O_2=Cu_2O$; (iv) 0·478 volt, $Q=50,400$ cal. for $Pb+\frac{1}{2}O_2=PbO$; (v) 0·855 volt, $Q=61,000$ cal. for the change $Ni+\frac{1}{2}O_2=NiO$; (vi) 0·897 volt, $Q=74,200$ cal. for the change $3FeO+\frac{1}{2}O_2=Fe_3O_4$; (vii) 1·040 volts, $Q=66,600$ cal. for the change $Fe+\frac{1}{2}O_2=FeO$; and (viii) 1·147 volts, $Q=26,750$ cal. for $C+\frac{1}{2}O_2=CO$. The potential and thermal values are, in general, in good agreement with the theoretical values and with those found from direct calorimetric determinations. Cupric oxide has an oxygen pressure of 0·21 atmosphere at 1008°, and 1 atm. at 1085°. Ferric oxide has an oxygen pressure of 0·21 atm. at 1322°, and 1 atm. at 1405°. Cuprous oxide has a pressure of 0·21 atm. at 1693°; lead oxide has an oxygen pressure of 0·014 mm. at 1200°. J. F. S.

The Ionisation of Sulphuric Acid and Neutral Potassium Sulphate in Aqueous Solutions of Moderate Concentrations. J. A. Muller (*Bull. Soc. chim.*, 1916, [iv], **19**, 438—441. Compare A., 1913, ii, 115).—By carrying out the electrolysis of solutions of sulphuric acid and potassium sulphate, each solution containing 1 gram-molecule per litre, under conditions such that the amount of the ions liberated at each electrode could be determined, the author shows that, in solutions of the above concentration, sulphuric acid is ionised to $2H^{\cdot}$ and SO_4'', and the potassium sulphate to $2K^{\cdot}$ and SO_4''. W. G.

Some Electrolyses. J. A. Muller (*Bull. Soc. chim.*, 1916, [iv], **19**, 441—444).—If an electrolytic cell is set up, the cathode being in a porous pot containing a molecular solution of sulphuric acid, and immersed in an outer vessel which contains the anode in a molecular solution of potassium hydroxide, on electrolysis the hydrogen liberated exceeds the sum of the hydrogen equivalent to the potassium which has travelled to the cathode and the SO_4'' which has passed to the anode, and the author considers that this is due to the potassium hydroxide being partly ionised to OK'

and H˙. If in the above cell the potassium hydroxide is replaced by hydrochloric acid, the hydrogen liberated at the cathode is in excess of the sum of the hydrogen equivalent to the hydrochloric acid decomposed and the SO_4'' which has migrated to the anode, this being due to the fact that, towards the end of the electrolysis, oxygenated compounds of chlorine, and, finally, free oxygen, are liberated at the anode, with the result that for every atom of oxygen thus set free a molecule of hydrogen is liberated at the cathode. If in a similar cell the anode cell contains a molecular solution of gold chloride, the only gases liberated are hydrogen at the cathode and oxygen, slightly ozonised, at the anode, there being no sêparation of gold. W. G.

Dependence of Transport Numbers on the Nature of the Solvent. F. Krüger (*Zeitsch. Elektrochem.*, 1916, **22**, 445—446).—A theoretical paper in which it is shown that the product $v\eta = c'$ and $u\eta = c''$, where v and u are the transport velocities of the anion and cation and η the viscosity-coefficient of the solvent. It is therefore held that the transport numbers will tend to the same value in all non-associated solvents, but in the solvents where the molecules are very large, that is, associated solvents, and in all cases where solvates are formed, the transport numbers will have very different values (compare following abstract). J. F. S.

Determination of the Transport Number of the Silver Ion in 0·01*N*-Silver Nitrate Solution in Mixtures of Ethyl Alcohol and Water at 40°. H. Krumreich (*Zeitsch. Elektrochem.*, 1916, **22**, 446—464).—The author has directly determined the transport numbers of 0·01*N*-silver nitrate solution in various alcohol–water mixtures at 40° by the direct Hittorf method. The following values were obtained: in pure water, 0·4820; 10% alcohol, 0·4821; 30% alcohol, 0·4881; 50% alcohol, 0·4586; 70% alcohol, 0·4464; 90% alcohol, 0·4210; and 99·8% alcohol, 0·4100. The concentration cells of various alcohol–water mixtures of 0·01*N*-silver nitrate were measured, and from the *E.M.F.* values obtained the transport numbers of the silver ion were calculated. The results in this case differed from the results of the direct measurements by from −5·0% to +2·6%. The direct method therefore gives the most trustworthy values, although the indirect method may be used as a control and for deciding whether any secondary reactions have occurred during the direct measurement. The author has, contrary to the results of Carrarra (A., 1903, ii, 708), been unable to show that such occur in his experiments, at least to such an extent that they would affect the value of the transport number. The specific conductivity of the various solutions used in this work was determined at 40° (compare preceding abstract). J. F. S.

Anodic Hydrogen Peroxide Formation During the Electrolysis of Malonates. C. Schall (*Zeitsch. Elektrochem.*, 1916, **22**, 422—423).—The author has electrolysed *N*-solutions of normal and acid sodium and potassium malonates at low temperatures.

The solutions were placed, either in an open apparatus or in a closed U-tube, and cooled with solid carbon dioxide and alcohol. The electrolysis took place between platinum electrodes by means of a current of 0·2—0·4 amp. with a terminal potential of 10 volts. After 0·25—0·5 amp. hour had been passed a quantity of the anode liquid was removed and analysed. This gave both the titanic acid and vanadic acid reactions for hydrogen peroxide, the colour in both cases increasing in intensity the lower the temperature and the longer the current had passed. A quantitative analysis indicated amounts of hydrogen peroxide from 5 to 20 mg. per 100 c.c. of anode liquid. Under analogous conditions, potassium succinate, phthalic acid, and sodium phthalate also yielded hydrogen peroxide at the anode. There was no production of hydrogen peroxide in the case of sodium acetate, and in the case of potassium benzoate in acetone–water a brown coloration was produced which made it impossible to test for hydrogen peroxide.

J. F. S.

Influence of Catalyst Poisons on the Photo-electric Sensitiveness of Platinum. F. Krüger and E. Taege (*Zeitsch. Elektrochem.*, 1915, **21**, 562—569).—The effect of the poisonous gases, hydrogen sulphide, hydrogen cyanide, carbon monoxide, carbon dioxide, and ammonia on the rate of electron discharge from plates of platinum, palladium, brass, nickel, magnetite, and silver, illuminated by a quartz mercury lamp, has been investigated. It is shown that the photoelectric sensitiveness of platinum is greatly reduced by charging it with the catalyst poisons, hydrogen sulphide, hydrogen cyanide, and carbon monoxide. The strongest effect is shown with hydrogen sulphide. In this case the original conditions cannot be regained by repeated washing with air and evacuation, so that in all probability a layer of platinum sulphide has been formed; this has been advanced as a reason for the catalytic poisoning of platinum by hydrogen sulphide. It is uncertain whether a similar state of affairs occurs with the other poisons. In this case, long evacuation or exposure to air causes a recovery of the sensitiveness of the platinum. This recovery would obviously take place more rapidly and be stronger if only a surface adsorption had occurred and if the photoelectric effect is produced from the surface layer. Gases diffuse, however, into the interior of the platinum, and much more so in the case of palladium. The penetrating depth of the photoelectric action is, however, only 3×10^{-6} cm. (Partzsch and Hallwachs, *Ann. Physik*, 1913, [iv], **41**, 247). Hence the actions in the deeper layers demand that the sensitiveness is dependent on the previous history of the platinum. Charging platinum with nitrogen has no effect, which is analogous to the absence of change in the catalytic and electrochemical effects when platinum is charged with nitrogen. Charging with carbon dioxide produces a slight increase in the photoelectric sensitiveness. Ammonia produces an increase in the sensitiveness, which is apparently contrary to what might be expected, since the catalytic activity of platinum in water formation is decreased by ammonia.

It seems, therefore, that in general a high photoelectric sensitiveness is connected with a strong catalytic action. J. F. S.

Variation of the Specific Heat of Gases with the Pressure. SILVIO LUSSANA (*Ann. Physique*, 1916, [ix], **6**, 344—356).—Polemical. A reply to Peczalski (compare A., 1916, ii, 216). W. G.

Relations between Thermal Properties. Molecular Coefficient and Constitution of Organic Compounds. STEFANO PAGLIANI (*Gazzetta*, 1916, **36**, ii, 310—334. Compare A., 1915, ii, 672, 819; 1916, ii, 291).—The investigations made on elements and inorganic compounds are now extended to organic compounds. Since, however, in most cases the values of the specific heats, especially at low temperatures, are unknown, the values of the entropy have not been calculated, but only the changes of the latter with change of state, that is, the quotient of the heat of fusion or vaporisation by the corresponding absolute temperature. Where direct measurements of the latent heats are lacking, the values obtained from cryoscopic and ebullioscopic measurements are employed.

The general rules obeyed are as follows: (1) For the members of a homologous series the variation of the entropy on fusion diminishes as the molecular-coefficient increases, the highest values of this coefficient usually corresponding with the lowest values of such variation; (2) with isomerides, the variation of the entropy on fusion is constant. That irregularities occur is regarded as due to the experimental difficulties attending the determination of the melting point and heat of fusion of organic compounds. It is found, further, that the values of the change of entropy on fusion, especially among the members of a homologous series, follow the order of magnitude of the changes in the specific volume on fusion, the latter measuring the degree of stability of form.

Rule (1) finds an exception in the series: benzene, toluene, xylene, and in derivatives of this series, but this ceases to be an exception if the higher homologues are regarded, not as alkylated benzenes, but as phenylated paraffin hydrocarbons.

In the case of vaporisation, the variation of the entropy also diminishes as the molecular-coefficient increases with the terms of a homologous series. In this case no exception to the general rule is presented by the series of benzene and its homologues or by derivatives of this series. With hydrocarbons belonging to different series and having equal molecular-coefficients, the variations of the entropy on vaporisation differ but little. With compounds containing carbon, hydrogen, and oxygen, and having equal molecular-coefficients, this variation has maximal values for the saturated alcohols, both aliphatic and aromatic, and minimal values for the saturated aliphatic acids. Almost exactly intermediate positions are held by the nearly equal values for esters and ketones.

For those series with which Trouton's law holds, expressions may be deduced of the following general form:

$$r/T = K/M = K/[(12+2)n + 16n_1 + 14n_2 \pm m],$$

where r is the heat of evaporation, T the absolute boiling point, K Trouton's constant, n, n_1, and n_2 the respective numbers of carbon, oxygen, and nitrogen atoms in the molecule, and m a positive or negative whole number. Thus, for the saturated hydrocarbons, $r/T=20/(14n+2)$, the value for methane being 1·250, which is of the same order of magnitude as the values, 1·430 and 1·341, for water and ammonia respectively; since $T=109°$, the heat of evaporation of methane becomes 136·25 (at $-164°$). This method may be applied generally to the calculation of the heat of vaporisation of compounds of any series for which Trouton's constant is known.

The relation deduced by Duclaux (A., 1913, ii, 104) is based on the universal application of Trouton's Law to all substances, simple and compound, mineral and organic. That this law does not exhibit such universal applicability is shown by the fact that compounds of different chemical functions, even when composed of the same elements and having the same molecular-coefficient, present marked differences in the values of the variation of the entropy accompanying change of state.

The values of the heats of vaporisation of various metals obtained by Wehnelt and Musceleanu (A., 1913, ii, 23) lead to values of the variation of entropy on vaporisation which agree satisfactorily with the periodic relation between variation of entropy and atomic-coefficient.

Taken in conjunction with Casale's expression for calculating approximately the boiling points of hydrocarbons of the methane series, the author's results lead to the formula $r/\Sigma(109{\cdot}2/n^a)$, for the variation of the entropy of a hydrocarbon on evaporation, n being the number of carbon atoms in the molecule. Since for isomerides the variation of the entropy is constant, it follows that the heats of evaporation of isomeric hydrocarbons will diminish as the boiling point falls, that is, as the number of hydrogen atoms in the nuclei diminishes and the number of substituent methyl groups increases.

The total heat of evaporation, being equal to the sum of the external and internal heats, may be expressed by the relation $r=Aup+1{\cdot}9878CT/M\,.\ln.(d/D)$, where A is the thermal equivalent of unit work, u the differential volume between vapour and liquid, p the pressure, C a constant for each substance, T the absolute temperature, D the density of the saturated vapour, and d the density of the liquid. Replacing D by $0{\cdot}08955M/2{\cdot}016$, the variation of the entropy may be expressed by $r/T=Aup/T+1{\cdot}9878C/M\,.\ln(d/0{\cdot}04477M)$. Since, for isomerides, the molecular volumes in the liquid state are equal (Kopp), the Dieterici constants at the boiling point exhibit close agreement, and the values of r/T are also equal, the conclusion is drawn that the values of u/T are constant for isomerides at constant pressure; in other words, the increase in volume on vaporisation of isomeric compounds is proportional to the absolute temperature of evaporation. Further, since the molecules are uniformly distributed and their number does not vary, the increase in volume on evaporation, representing

the increase of distance between the molecules, is, at any rate for isomeric compounds, proportional to the absolute boiling point. Consequently, as has been previously found, the heats of evaporation of isomerides are proportional to the absolute boiling points.

Of twenty-one organic compounds for which the heats of fusion and evaporation are known, only three or four obey approximately de Forcrand's expression (A., 1903, ii, 267, 353, 409, 466), the so-called constant varying from 20·7 to 40 (compare A., 1916, ii, 291; also Massol and Faucon, A., 1909, ii, 791; 1911, ii, 852).

T. H. P.

Mixtures. FÉLIX MICHAUD (*Ann. Physique*, 1916, [ix], **6**, 223—344).—In the first part of the paper, which is mathematical, the author deduces certain theorems governing the laws of mixtures. From the energy point of view, entropy may be considered as an independent constituent, for which semi-permeable walls can be imagined, and it is capable of exercising an osmotic pressure, this osmotic pressure being a measure of the thermodynamic potential. He then puts forward a theorem by means of which it is possible, without any intermediate calculation, to ascribe to any given thermodynamic system a simple system of equations in which each phase is represented by an equation, each component being represented by a single term in each equation. This theorem permits of the reconstruction, in a simple and rapid manner, of the principal results of the thermodynamics of mixtures (Clapeyron's equation, law of mass action, etc.). A generalised Clapeyron equation may be deduced which contains other formulæ previously considered as distinct. The demonstration of the fact that a monatomic gas is necessarily an inert gas results immediately from this method of considering the subject. One entirely new fact to which this mode of calculation leads is the theorem of solid substances in excess. Thus, in a system comprising a liquid phase, which contains volatile and non-volatile components, suppose that there exists, in addition, a gaseous phase, formed entirely of the volatile components of the liquid phase, and that the non-volatile components are dissolved to saturation in the liquid phase and form each, in the pure state, a solid phase, then, in the equation relative to the liquid phase, the terms relative to the non-volatile components can be neglected.

In the experimental portion of the paper an account is given of a systematic study of the different methods by which the vapour pressure of a mixture can be measured, and the mixed vapour analysed. The two processes are best carried out separately in two distinct pieces of apparatus. The first apparatus, which is a pressure gauge with eleven tubes, permits of the construction, at one experiment and quite accurately, of the total vapour-pressure curve of a mixture of volatile liquids. The mixtures studied were ether–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) naphthalene, (*c*) camphor; formaldehyde–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) naphthalene; acetone–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) acetanilide; ether–chloroform, and the same

saturated with (*a*) picric acid, (*b*) acetanilide, (*c*) naphthalene. The results are set out in detail and the curves figured, and they verify the theorem of solid substances in excess, and also lead to the result that the presence of a substance dissolved to saturation tends to make the curve of total pressure more nearly rectilinear. W. G.

Use of Shukov's Apparatus for Molecular Weight Determinations. GEORG VON KOZICKI and ST. VON PILAT (*Zeitsch. angew. Chem.*, 1916, **29**, i, 423—424).—Shukov's apparatus can be used for the determination of molecular weights of dissolved substances when a solvent of relatively high freezing point is used. The method of carrying out the determinations is similar to that used, with the same apparatus, for the determination of freezing points; a Beckmann thermometer cannot be utilised.

The results obtained with ten different solutes, using naphthalene as solvent, are given, and are very satisfactory. T. S. P.

Calorimetry by Combustions with Sodium Peroxide. W. G. MIXTER (*Amer. J. Sci.*, 1917, [iv], **43**, 27—34).—An account is given of the apparatus and of the manipulation involved in the use of sodium peroxide as an oxidising agent in thermochemical determinations. H. M. D.

Physico-chemical Force of Attraction. III. L. G. GURVITSCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 856—861. Compare A., 1914, ii, 435; 1915, ii, 744).—The phenomenon of the autodisintegration of floridin which occurs in various liquids necessitates the assumption that the force of physico-chemical attraction which tears off small particles from the surfaces of the floridin granules is capable of similar behaviour at the surface of other substances, such as metals. Experiment shows, indeed, that metals do undergo pulverisation when shaken in the form of granules or small pieces with various liquids at the ordinary temperature. Between the degree of disintegration of the metal and the residual chemical energy of the liquid, measured by the heat of adsorption, perfect parallelism exists, and the conclusion is drawn that the pulverisation is caused by the physico-chemical force of attraction between metal and liquid. This force is alone insufficient to tear particles from the compact surface of the metal, but becomes able to do so when the impacts of the metallic fragments loosen the surface layers.

The shaking of certain liquids of specially great residual energy, such as water, methyl alcohol, acetone, etc., with metals may even lead to the formation of colloidal solutions of the metals of very considerable concentration and marked stability. The maximal percentage concentrations of the colloidal solutions obtainable on shaking 100 grams of granulated lead with 120—130 c.c. of various liquids are: water, 0·098; methyl alcohol, 0·132; ethyl alcohol, 0·0134; amyl alcohol, traces; acetone, 0·0115; pinene, 0·0088; and aniline, 0·0071. In methyl alcohol, colloidal solutions of the following percentage concentrations are obtainable: cadmium, 0·052; zinc, 0·0028; bismuth, 0·059; mercury, 0·032; and tin, 0·0031.

This procedure furnishes a very simple method for obtaining colloidal metal solutions, but it is attended with some uncertainty, which appears to be due to insufficient cleanness of the surface of the vessel in which the shaking takes place. The best results are obtained if the vessel is washed successively with chromic–sulphuric acid mixture, water, alcohol, and several times with the liquid to be employed; it should then be charged at once and closed. Excessive shaking may result in the complete deposition of the metal from the colloidal solution. T. H. P.

Surface-tension Tables from Data by Traube and Forch. R. Somogyi (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, **3**, 60—70).—The tables give the densities and capillary constants of various alcohols, aldehydes, acids, bases, salts, etc. H. W. B.

Influence of the Quantity of the Adsorbent, Aluminium Hydroxide, on the Adsorption of Aqueous Solutions of Hen's Egg-albumin of Constant Concentration. M. A. Rakuzin and (Mlle.) Ek. Maks. Braudo (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 461—465).—The adsorption of egg-albumin in 7·05% solution by proportions of dry, commercial, precipitated aluminium hydroxide varying from 15% to 1·875% of the weight of the solution has been investigated. When the proportion of adsorbent is below a certain minimum, no adsorption takes place, but increase of the adsorbent to 13% is then accompanied by rapid increase in the percentage of the total albumin adsorbed to a maximum of about 20%. The latter value is not increased by addition of a further quantity of adsorbent to the solution.
T. H. P.

Protein Substances and Anti-substances as Products of Adsorption. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 465—468).—From analogy with the separation into toxin and anti-toxin occurring when anti-diphtheritic and other serums are treated with adsorbents (compare Ostromisslenski, A., 1915, i, 751, 752; Zunz, *Zeitsch. Immunitätsf.*, 1914, 326), the author regards the separative adsorption of proteins, enzymes, etc., by aluminium hydroxide as separation into an adsorbed portion and a non-adsorbed anti-substance. Thus, hen's egg-albumin, $[\alpha]_D$ $-37·1°$, yields 19·22% of adsorbed albumin I, $[\alpha]_D$ $-56·0°$, and 80·78% of "anti-albumin," $[\alpha]_D$ $-32·6°$; hen's egg-albumin peptone, $[\alpha]_D$ $-95·24°$, gives 24·19% of adsorbed peptone I, $[\alpha]_D$ $-156·68°$, and 75·81% of "anti-peptone," $[\alpha]_D$ $-75·0°$; and diastase (optically inactive) yields 7·10% of adsorbed diastase I and 92·90% of "anti-diastase," the latter, but not the former, giving Ostromisslenski's reaction with picramic acid. In the case of the solid paraffins of Grosny naphtha, adsorption effects removal of the lower homologues present, and it may be assumed that the adsorbed fractions of proteins, enzymes, and serums are also of lower molecular weight than the non-adsorbed fractions remaining in solution.
T. H. P.

Retarded Diffusion and Rhythmic Precipitation. J. STANSFIELD (*Amer. J. Sci.*, 1917, [iv], **43**, 1—26).—An account is given of earlier work on the formation of rhythmic precipitates, and further experiments are described in which the author has investigated more particularly the phenomena associated with the precipitation of silver chromate by diffusion of silver nitrate and potassium chromate, when one of the reagents is in the form of an aqueous solution and the other in the form of a gelatin jelly.

The results obtained show that separated bands of precipitate are most readily produced when a concentrated silver nitrate solution diffuses into a weak chromate solution. The diffusion of a strong chromate solution into a weak silver solution yields similar results, but the particles formed are larger. When the concentrations of the two reagents approximate to equality, the precipitate appears to be continuous, but under the microscope it is seen to be finely banded.

The gradual increase in the distance between the bands during the process of rhythmic precipitation has been attributed to progressive dilution, but it seems that the rate of diffusion is an important factor. The rates of diffusion of different substances in gelatin vary considerably, and a strong solution diffuses more rapidly than a weak solution. The rate of diffusion of a given aqueous solution is retarded by increasing the concentration of the jelly, and the total range of diffusion is also diminished by this increase in the jelly concentration. H. M. D.

Molecular Condition of Pure Liquids. P. N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1008—1032).—The author develops methods of investigating the molecular state of liquids and saturated vapours based on the properties of the thermodynamic functions, and the principles of the theory of corresponding states, independently of any particular form of the equation of state.

Proof is advanced of the following so-called "capillary–chemical law of equimolecular surfaces": With all normal liquids forming, at corresponding temperatures, disperse systems with equimolecular surfaces (systems of equimolecular degrees of dispersion), the free molar surface energies are proportional at corresponding temperatures. This relation may be expressed conveniently in the form $(\gamma v^n/T)$(corres.) = a universal constant $= c$, γ being the surface tension, v the molecular volume (M/d), n an arbitrary number, and T the absolute temperature; for corresponding values of T, the values of c for different liquids should be dependent, not on the chemical nature of the compound, but only on the temperature. Introduction of different values for n into this equation leads to a number of universal constants, c_0, c, c_1, c_2, etc., and normal liquids should satisfy each of the relations thus obtained.

Further, $d(\gamma v^n)/dT = k$, that is, the thermal coefficient of the molecular free surface energy for all disperse drops of a system with equimolecular surfaces, is constant, independently of the chemical nature of the substance. Integration of this expression

within the limits from the critical temperature to a temperature very near to it leads, on the assumption that $\gamma=0$ at the critical temperature, to the equation $\gamma v^n/(T_c-T)=A$, A being also a universal constant, independent of the chemical nature of the compound, but dependent on the temperature. Substitution for n of the values 0, 2/3, 1, 2, etc., gives expressions for a series of universal constants, A_0, A, A_1, etc., each of which should be satisfied by normal liquids.

Investigation of the values of the functions $\gamma v^n/T$ and $\gamma v^n/(T_c-T)$ for a number of liquids shows that the following liquids are abnormal: (1) *n*-octane, *m*-xylene, mesitylene, durene, naphthalene, diphenylmethane, αβ-dibromoethane; (2) methylaniline, dimethylaniline, acetonitrile, propionitrile; (3) acetone, anisole, and phenetole; (4) water, methyl, ethyl, propyl, *n*-butyl, *iso*butyl, and *iso*amyl alcohols; (5) acetic, propionic, *n*-butyric, *iso*butyric, and *iso*valeric acids; (6) methyl acetate, methyl and ethyl propionates, methyl butyrate and *iso*butyrate; (7) bromine, nitrogen tetroxide, carbon disulphide, and silicon tetrachloride. Ethyl ether and carbon tetrachloride are normal liquids, as also is propyl formate in the temperature interval 0·6054—0·8464.

T. H. P.

Relation between the Physical Properties of Solutions and their Mixtures. ERIK ANDERSSON (*Medd. Nobel Inst.*, 1916, **3**, No. 12, 1—22).—It is shown that the mixture rule is applicable to mixtures of solutions of different electrolytes containing a common ion, and that the calculated values of the density, electrical conductivity, surface tension, coefficient of expansion, and freezing-point depression are in close agreement with those found by experiment. The mixture rule is also applicable in respect of the density when solutions of sucrose are mixed with various salt solutions, but such mixtures do not satisfy the mixture rule in respect of the freezing-point depression. H. M. D.

Structure of True Solutions and Nature of the Transformations Occurring in Them. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 532—537).—In this communication, the following points, to be dealt with in detail later, are briefly considered.

When solutions (about 1%) of oleates of various metals in xylene are heated from the ordinary temperature to the boiling point, the following changes of colour occur: nickel oleate, green $\rightleftarrows$ greenish-yellow $\rightleftarrows$ yellow (b. p.); chromium, violet $\rightleftarrows$ green; iron, orange $\rightleftarrows$ orange-red; cobalt, red $\rightleftarrows$ violet $\rightleftarrows$ lilac $\rightleftarrows$ blue $\rightleftarrows$ indigo (b. p.); these colour changes occur suddenly as the temperature changes, and are perfectly reversible. Similar series of colour changes are produced in aqueous solutions of the chlorides of the same metals either by heating or by saturation with hydrogen chloride, but most of the theories advanced to explain this phenomenon, for instance, those based on the assumption of hydration

or ionisation, are inapplicable to solutions of anhydrous oleates in completely anhydrous aromatic hydrocarbons.

According to the author's theory, such colour changes in true solutions are due to changes in the magnitude of the intensity factor of the volume energy of the molecules, that is, of their condensation, which is often accompanied by reactions of combination or decomposition. The change in this intensity factor may be caused by different kinds of energy, for instance, thermal, volume (great contraction) or chemical (solvation, desolvation, solventolysis, hydrolysis, and the like) energy, and identical changes in the intensity factor of the volume energy of the molecules exert identical effects on the absorption of light energy by the solutions, quite independently of the kind of energy causing the changes.

Complete parallelism exists between the colours of dispersoid solutions of the chlorides, and their hydrates and hydrochlorides, of copper, nickel, cobalt, iron, and chromium in aromatic hydrocarbons, and those of true solutions in the same compounds. From the experimental data obtained, the following conclusions are drawn: (1) True solutions undoubtedly possess a granular structure, that is, are disperse, their stability being due to causes given in the author's dispersoidological theory of true solutions (A., 1913, ii, 678). (2) Investigation of dispersoid solutions of coloured salts represents a powerful agent for the elucidation of the nature of true solutions, and permits of the determination of the chemical or physical transformations responsible for the changes in colour.

The weaker the base combined with oleic acid in an oleate, the more readily soluble is the oleate in aromatic hydrocarbons, and the more nearly does the solution obtained approach typical true solutions, both in degree of dispersiveness and in other properties. In other words, in an oleate containing a weak base, the property of oleic acid of dissolving (and solvating) in aromatic hydrocarbons is weakened to a less extent than in an oleate containing a stronger base (compare A., 1916, ii, 177).

The bearing of these considerations on the causes underlying the solubility and insolubility of substances is discussed.

T. H. P.

The Actual State of the Theory of Electrolytic Dissociation in Water and Non-aqueous Solvents. BOHDAN DE SZYSZKOWSKI (*Medd. Nobel Inst.*, 1916, **3**, No. 11, 1—16).—The formula proposed by the author (A., 1915, ii, 616) to express the relation between the degree of ionisation and the concentration of an electrolyte is shown to be equivalent to the formula put forward by Kraus and Bray (A., 1913, ii, 914). In the latter, however, the deviation from the law of mass action is attributed to the influence of the ions, whilst the author's formula,

$$c\alpha^2/(1-\alpha)=K+k(c_0^{1/3})^m,$$

ascribes the deviation to the influence of the undissociated molecules, the concentration of which is given by $c_0=c(1-\alpha)$.

Analysis of the equation leads to the conclusion that the existence of a minimum value of α requires that the constant K should

be comparatively large, this minimum being the resultant of the effect produced by the operation of the law of mass action as measured by K and that produced by the action of the undissociated molecules as measured by $k(c_0^{1/3})^m$.

From an examination of the data recorded by Kraus and Bray for non-aqueous solutions, it is found that the product of the constant m and the specific inductive capacity ϵ has approximately the same value for all solvents. According to Walden, the linear concentration $c^{1/3}$, corresponding with the minimum value of the degree of ionisation, is also related to the specific inductive capacity of the solvent in accordance with the equation $\epsilon/c^{1/3}=$constant, and by continuing these relations the author arrives at the equation $m.c^{1/3}=$constant. In other words, the constant m in the above ionisation formula varies inversely as the distance between the molecules of the electrolyte in the solution, which shows a minimum conductivity.

Although Kraus and Bray have assumed that the ionisation curve on both sides of the minimum is represented by the above equation, the actual observations seem to show that a more complex expression is required to give a complete account of the ionisation relations. This may be done by an equation of the type $c\alpha^2/(1-\alpha)=k_m(c_0^{1/3})^m+k_n(c_0^{1/3})^n+K$, in which $m>3$ and $n<3>0$. In this equation, the first term determines the behaviour of the electrolyte in concentrated solution, whilst the second and third terms regulate the behaviour in dilute solution. This equation, in combination with $m\epsilon=$constant, leads to the conclusion that the concentration of the solution at which the minimum conductivity occurs is the greater the greater the specific inductive capacity of the solvent. H. M. D.

Influence of Electrolytes on the Dissociating Power of Solvents. III. A. N. SACHANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 361—372. Compare A., 1914, ii, 419; 1915, ii, 526, 732).—Cryoscopic measurements on solutions of dimethylpyrone and hexachloroethane in aniline give for the latter the cryoscopic constant 63·5—63·8, the value calculated from the latent heat of fusion being 67·5. The low value obtained by Ampola and Rimatori, namely, 58·7 (A., 1897, ii, 306), is due to the formation of complexes.

The molecular weights of pyridine and aniline in acetic acid, as determined cryoscopically, are comparatively little above the normal values, although the increase of the molecular weight with the concentration, particularly for aniline, is clearly marked.

According to the hypothesis which assumes the formation of complexes able to conduct, a normal magnitude of the coefficient i or of the molecular weight on abnormal dissociation is indicative of marked electrolytic dissociation of polymeric molecules. Further, this hypothesis leads to the conclusion that the freezing-point depression of a mixture of two electrolytes, possessing on abnormal dissociation normal molecular weights, should be the sum of the two partial depressions of the separate electrolytes. Actual experi-

ment shows that the depression of a mixture of pyridine and aniline acetates in acetic acid is, within the limits of experimental error, additive; only for quite concentrated solutions is the measured depression a little greater than the calculated value, probably owing to solvation. The molecular weight of potassium formate in acetic acid is considerably less than the normal value, the formic acid being replaced by acetic acid in the salt; the extent to which this replacement proceeds increases with the dilution of the salt, so that in dilute solutions the molecular weight is approximately one-half of the calculated value. Only one mixture of potassium formate and pyridine acetate in acetic acid was examined, additivity of the partial depressions being observed.

These results support the formation of conducting complexes, and are in contradiction to the hypothesis which assumes a dissociating influence of the ions on neutral molecules. T. H. P.

The Phenomena of Suspended Transformation. GERTRUD KORNFELD (*Monatsh.*, 1916, **37**, 609—633).—After reviewing the arguments for and against the existence of a metastable region for supercooled liquids and supersaturated solutions, in which crystallisation will not occur spontaneously, but needs the presence of a suitable nucleus, the result is given of a large number of experiments on the crystallisation of salol in sealed glass tubes at 25° and 30°. As a result of the investigation, the conclusion is drawn that, in the majority of the tests made, crystallisation occurred spontaneously, the influence of impurities being evident only in a very small proportion. At the temperatures used, gentle agitation is insufficient to induce crystallisation, so that the observations do not favour the idea of a metastable region, and appear to confirm the views of Pfaundler (this Journal, 1877, i, 433, 435) and de Coppet (this Journal, 1876, i, 184) of spontaneous crystallisation as dependent on kinetic molecular conditions. D. F. T.

The Existence, Size, and Determination of Crystal Molecules. A. FOCK (*Centr. Min.*, 1916, 392—396).—The author argues in favour of the existence of chemical molecules as such in crystals, as opposed to the theory, supported by *X*-ray analysis, that atoms or electrons are situated at the points of the point-systems in crystal structures. L. J. S.

Table of Schoenflies's Cubic Space-lattices. PAUL NIGGLI (*Centr. Min.*, 1916, 497—505).—Schoenflies's thirty-six space-lattices are reduced to nine types of point-systems and are represented in a table. Examples are given of how various cubic substances conform with these structures when the atoms or ions (groups of atoms as suggested by *X*-ray analysis) are situated at the points of these point-systems. L. J. S.

Theory of Peptisation. WILDER D. BANCROFT (*J. Physical Chem.*, 1916, **20**, 85—117).—A theoretical paper, in which peptisation is critically considered. Accepting Freundlich's generalisation

that adsorption involves a lowering of the surface tension of the adsorbing phase, the author puts forward the following as a theory of peptisation. Any substance which is adsorbed by a second will lower the surface tension, and will therefore tend to disintegrate, in other words, to peptise it. Should the Freundlich generalisation prove not to be universally true, such a theory may be easily modified to account for new facts. The theory being accepted, it follows that peptisation may be brought about by a solvent, by a dissolved non-electrolyte, by an ion, by an undissociated salt, and by a colloid. Adsorption decreases in general with rising temperature, and so does the cohesion of the adsorbing substance. Hence peptisation may be brought about by a solvent at high temperature even when it does not occur at low temperatures. As instances of this, the author discusses the cases: glass–water, vulcanised rubber–organic solvents, and gelatin–water. As cases of peptisation by a dissolved non-electrolyte, the author discusses sugar or glycerol and hydroxides in water, and ether and pyroxylin in alcohol. Typical cases of ion peptisation in water are silver bromide and potassium bromide, silica or chromic oxide and potassium hydroxide, alumina and acids, and chromic oxide and chromic chloride. No case of peptisation by a soluble undissociated salt has been studied as such, but if impure mercury is shaken with water, peptisation is brought about by the oxide film. As typical cases of peptisation by a colloid in water, silver bromide–gelatin, alkaline chromic oxide–hydrated ferric oxide, and gold–stannic oxide are quoted and discussed. Since adsorption depends on the surface, and since peptisation involves breaking down the cohesion of particles, there is no necessary connexion between the amount of adsorption and the ease of peptisation. A coarse-grained, porous precipitate may be peptised more readily than the same mass of substance in a more dense form. Von Weimarn's theory of peptisation, which assumes that the solid always dissolves in the peptising agent, forming unstable compounds which then break down the precipitate forming a sol, is discussed and shown to be inadequate. J. F. S.

Viscosity and Hydration of Colloidal Solutions. SVANTE ARRHENIUS (*Medd. Nobel Inst.*, 1916, **3**, No. 13, 1—20).—The fact that the viscosity of many colloidal solutions changes more rapidly than the concentration is not in agreement with Einstein's formula, and Hatschek has expressed the view that this is due to the formation of an envelope of the dispersive medium round each particle of the disperse phase. When the quantities of water associated with the colloidal particles are calculated for various solutions, numbers are obtained which are difficult to reconcile with the chemical relations between the disperse phase and the dispersive medium.

The data for colloidal solutions of sulphur and various proteins have accordingly been re-examined, and it is found that the experimental observations can be simply interpreted in terms of the author's formula for the viscosity of mixtures as modified by Kendall (A., 1914, i, 109). In the case of sulphur sols, the formula may be applied directly with entirely satisfactory results, but for

solutions of proteins it is necessary to assume that the molecules are hydrated to some extent. The combined water per gram of protein varies from 0·7 gram for egg-albumin to 2·2 grams for euglobulin. These quantities of water are much smaller than those obtained on the basis of Hatschek's hypothesis.

The fact that this hypothesis leads to the conclusion that the size of the water envelope is approximately proportional to the change in the viscosity produced by the addition of 1 per cent. of protein, is also said to afford internal evidence that it cannot afford a basis for the determination of the degree of hydration of colloids.

H. M. D.

Relation between the Colour and the Degree of Dispersion of Particles in Coloured Solutions. W. HARRISON (*J. Soc. Dyers*, 1917, **33**, 7—9).—A criticism of Ostwald's view (A., 1911, ii, 868) that the colour of colloidal solutions varies with the size of the particles, and changes in the direction yellow—red—blue, with increase in the size of the particles.

If acid is added gradually to a colloidal solution of night-blue free base, it first dissolves with very little change in colour, is then precipitated without colour change, and finally redissolves with change in colour through green to yellow. Similar behaviour is exhibited by Victoria-blue B, Nile-blue, acid-violet 7B, and formyl-violet S4B. These changes are not in accordance with Ostwald's rule.

If the above dyes are dissolved in glacial acetic acid, they change in colour in the direction violet—blue—green—yellow on the addition of mineral acids, but there is no visible change in the size of the particles. The amount of mineral acid required is much less than in aqueous solution.

In the author's opinion, change in colour is more probably due to molecular rearrangement, and not to change in the size of the molecular aggregate, although it is possible that these changes may occur simultaneously. H. M. D.

Protective Colloids. IV. Radix Althaeæ as Protective Colloid. A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1916, **19**, 230—234. Compare this vol., ii, 21).—The protective action of extracts of the root of marsh mallow on solutions of colloidal gold, obtained by the reducing action of hydrazine hydrate, pyrogallol, catechol, and tannin, has been examined in detail. The increase in stability of the gold solutions in presence of the protective colloid is much less marked than that found in previous experiments with other plant extracts. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. A. GUTBIER and A. WAGNER (*Kolloid Zeitsch.*, 1916, **19**, 235—241).—The preparation of colloidal solutions by extracting quince seeds with water is described. The stability of the solutions has also been examined, with special reference to the influence of time, concentration, temperature, salts, acids, and alkalis.

H. M. D.

Ultra-microscopic Investigation of Tanning Phenomena in Jellies. W. MOELLER (*Kolloid Zeitsch.*, 1916, **19**, 205—213).—An account is given of the ultra-microscopic structures which are exhibited by gelatin jellies when these are subjected to the action of alcohol, tannin, chromic salts, and formaldehyde. The micro-photographic records show that the phenomena associated with the action of these reagents on jellies are closely similar to those which are characteristic of the tanning of hide fibres. The actual differences are due solely to the circumstance that the fibrils in the hide are orientated, whilst those in the jelly are distributed in all possible directions. It is assumed that gelatin contains two substances, α- and β-gelatin, of which only the α-gelatin forms the structural units, whilst the β-gelatin is structureless and occupies the spaces between the fibrils of α-gelatin. In the jelly these fibrils are independent of one another, and under the influence of external forces, the irregular net-work may be transformed into a system in which the fibrils are orientated, and in this way structures are developed which vary according to the nature of the forces to which the gelatin jelly is subjected. H. M. D.

Internal and Surface Structures in Jellies. I. W. MOELLER (*Kolloid Zeitsch.*, 1916, **19**, 213—219. Compare preceding abstract).—The author has examined the structure of gelatin subjected to the action of water vapour and warm water, of gelatin jellies before and after dehydration, and also the structure of gelatin which has been heated to a temperature at which it begins to decompose or has been subjected to the action of superheated steam and subsequently drawn out into threads.

The observations afford evidence in support of the view that gelatin consists of an irregular conglomerate of fibrils forming a network of α-gelatin with β-gelatin in the intervening spaces. The structure becomes visible when the gelatin is subjected to any action which removes the β-gelatin partly or completely. In these circumstances the fibril units of α-gelatin undergo orientation to a greater or less extent, forming fibril groups which are visible in the ultra-microscope. H. M. D.

Imitation of Certain Anatomical Structures. MARTIN H. FISCHER and MARIAN O. HOOKER (*Kolloid Zeitsch.*, 1916, **19**, 220—230. Compare A., 1916, i, 693; ii, 557).—A description is given of certain morphological structures shown by colloids or mixtures of colloids which have been subjected to hydration or dehydration. Attention is directed to the close resemblance between these and the structure of various forms of differentiated protoplasm in the living organism, and it is suggested that this differentiation of living protoplasm may be brought about by influences similar to those which are found by experiment to produce differences in the structure of simple colloids. H. M. D.

Non-, Uni- and Bi-variant Equilibria. X. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 514—527. Compare A., 1916, ii, 476).—A further discussion of

equilibrium relation in which it is shown that three types of pressure–temperature diagrams may be differentiated.

H. M. D.

The Equilibrium Solid–Liquid–Gas in Binary Systems which Present Mixed Crystals. IV. H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 555—564).—In a previous communication (compare this vol., ii, 81), it was shown that the coexistence of solid, liquid, and vapour in the system in which bromine and iodine are the components was characterised by the pressure–temperature curve showing two maxima and a minimum. In this system, the compound IBr is formed, and this forms mixed crystals with the components, but it is shown that this type of pressure–temperature curve may also be obtained when mixed crystal formation does not occur.

H. M. D.

Principle of the Change of an Equilibrated System under the Influence of an External Agent. II. E. VOLCHONSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 272—278. Compare A., 1912, ii, 441).—An analytical proof is given of the principle: Within an equilibrated system, subjected to external influence, all the processes which occur, taken either together or singly, are of such sign that they aid the work of the external factor.

T. H. P.

Equilibrium between Mucic Acid and its Lactones. W. A. TAYLOR and S. F. ACREE (*J. Physical Chem.*, 1916, **20**, 118—120).—A preliminary paper in which experiments, designed to determine the equilibrium conditions of acid and lactone in aqueous solution, are described. Quantities of mucic acid in excess were placed in water, and heated (*a*) at 30° for an hour, (*b*) at 100° for thirty minutes, and (*c*) kept at the ordinary temperature for some time. The solutions were then placed in a thermostat at 25°, and filtered portions withdrawn at intervals. The free acid was determined by titration in ice-cold solution with standard alkali solution, and the amount of lactone by adding an excess of $N/10$-standard alkali, boiling for a few minutes, and then titrating the excess of alkali with $N/10$-hydrochloric acid. The experiments show that the same equilibrium is reached in all three cases, the cases (*b*) and (*c*) requiring 1440 hours, and (*a*) requiring 2880 hours, on account of supersaturation. At equilibrium, there were roughly twice as many lactone groups as carboxyl groups in the solution. The data are insufficient to indicate whether the lactone present is a monolactone or a dilactone.

J. F. S.

Erroneous Interpretation of the Kinetics of Chemical Reactions. A. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 456—457).—If, in a reaction of the first order, A mols. of the reacting substance are taken in V litres of solution, and x mols. undergo change in time t, the velocity of the reaction is expressed

by the equation $-d[(A-x)/V]/dt=K(A-x)/V$ (i). When the volume remains constant, this equation gives

$$-1/V.d(A-x)/dt=K(A-x)/V \text{ or } dx/dt=K(A-x) \text{ (ii).}$$

If, however, the volume is not constant, either because there is an actual change or because the volume occupied by the reacting molecules requires a correction, equation (ii) is inapplicable, equation (i) becoming $dx/dt=(A-x)(K-1/V.dv/dt)$ (iii). Similar relations hold for reactions of higher orders. The author points out that equation (ii) has been erroneously employed by various investigators in cases where the volume varies, and where, consequently, equation (iii) should be used. T. H. P.

Time Reaction of the Neutralisation of Carbonic Acid and the True Dissociation Constant of Carbonic Acid. A. THIEL (*Zeitsch. Elektrochem.*, 1916, **22**, 423—424).—Polemical. The author criticises the work of Pusch (A., 1916, ii, 477, 557), and claims the field of work entered by Pusch as his own. Reference is made to work by the author and Strohecker (A., 1913, ii, 199; 1914, ii, 361, 448), and also by Strohecker (A., 1916, ii, 522).
J. F. S.

Reaction between Amylene and Trichloroacetic Acid in Different Solvents. II. G. E. TIMOFEEV and V. A. KRAVCOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 985—993. Compare A., 1915, ii, 755).—Oxygenated solvents form with trichloroacetic acid more or less stable solvates, and thus play the part of weak bases. In order to ascertain the effect of non-oxygenated basic compounds in this direction, the authors have investigated the change caused in the extent to which the reaction,

$$CCl_3{\cdot}CO_2H+C_5H_{10} \rightleftarrows CCl_3{\cdot}CO_2{\cdot}C_5H_{11},$$

occurs in the indifferent solvent, benzene, by the presence of dimethylaniline, pyridine, or diphenylamine; the experiments were made at both 25° and 50°.

At either temperature, the reaction is considerably checked by the addition of the first portions of dimethylaniline, the effect being greater than with oxygenated solvents, as would be expected from the higher basicity. As the proportion of added base increases, the curves for 25° and 50° exhibit a distinct tendency to approach and cut, as has already been found for acetone and for methyl ethyl ketone (*loc. cit.*). The effect is very nearly proportional to the proportion of base added, the curves approximating closely to straight lines. Similar results are obtained if the dimethylaniline is replaced by pyridine.

With diphenylamine, different results are yielded. In agreement with the much feebler basicity, the effect is here much less marked than in the previous cases, and the curves are more nearly similar to those of oxygenated solvents. The curves at 25° and 50° are perfectly parallel, the distance between them being about 11%, which is the same as for pure benzene at the same temperatures.

The conclusion is drawn that the amount of the acid falling to the share of the diphenylamine is constant, independently of the temperature, that is, that the complex which the base forms with trichloroacetic acid is stable as regards temperature. T. H. P.

Velocity of Solution of Metals. II. Velocity of Solution of Zinc in Acids. M. CENTNERSZWER (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 470—524. Compare A., 1915, ii, 562, 563). —A number of further results have been obtained, the principal ones being as follows.

Etched zinc dissolves in hydrochloric acid more rapidly than zinc with a polished surface. The metal, which reaches its maximum velocity of dissolution in 2*N*-hydrochloric acid, dissolves in fresh acid with a continually diminishing velocity, and the process of solution follows Boguski's law. Sulphuric acid dissolves zinc appreciably more slowly than does hydrochloric acid with an equal concentration of hydrogen ions.

Zinc sheets from one and the same melt dissolve with different velocities, owing to variations in the crystalline structure of the metal, but with rolled zinc sheets, concordant results are obtained. Zinc which has been treated with emery dissolves more rapidly than polished zinc, and zinc plates subjected to the action of iodine solution more rapidly than fresh plates.

The velocity of dissolution of the metal increases more rapidly than the concentration of the acid, and the black precipitate which forms at the surface of the metal during the action accelerates dissolution, removal of this precipitate resulting in the loss of the former activity of the metal. In distilled water, zinc retains its activity for a long time, but in the air the metal partly loses its activity. When rapidly cooled, zinc exhibits a more pronounced induction period than when slowly cooled, but if its surface is subsequently etched, its velocity of dissolution is the same as in the latter case. Prolonged heating at 400° of zinc which has been rapidly cooled increases its period of induction. The potential of active zinc is somewhat higher than that of passive zinc.

In order to explain the phenomena observed, the supposition is made that ordinary (chemically pure) zinc is in a passive condition, increase of the velocity of dissolution during the period of induction being explained by transformation of the metal from the passive to the active state.

An attempt is made to explain the passivity of iron and other metals in accordance with Helmholtz's theory of the electric double layer, and it is shown that such a representation is capable of furnishing explanations of: the influence of foreign metals on the solution of zinc (De la Rive's theory), the influence of mechanical and chemical treatment of the surface of the zinc, the period of induction, periodic phenomena in the dissolution of metals (Adler's theory, A., 1912, ii, 891), the passivification of metals by means of oxidising agents and polarisation, rusting of iron and other metals (compare Walker, Cederholm, and Bent, A., 1907, ii, 875; Cush-

man, *Elektrochem. Metallurg. Ind.*, 1907, **5**, 257, 365), the activation of metals by hydrogen (compare Grave, A., 1911, ii, 896), the specific influence of different electrolytes on the condition of metals, etc. T. H. P.

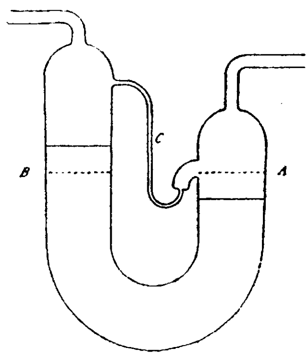
Rhodium Catalysis of Formic Acid. PH. C. WLADISLAW HAAS (*Zeitsch. Elektrochem.*, 1916, **22**, 443—445).—The author is of the opinion that the catalytic activity of the noble metals is to be attributed to electrochemical actions, and to confirm this view the decomposition voltage of formic acid has been determined between electrodes of various types and sizes. A 30% solution of formic acid was used in all experiments; with two bright electrodes, irregular decomposition curves were obtained, but no definite decomposition voltage could be observed. Using two platinised electrodes, the nature of the curves changed, and a definite value of 0·24 volt was obtained for the decomposition voltage. It was also found that if the anode alone was platinised, a definite value could be obtained for the decomposition voltage. Using two platinsed electrodes which were covered with activated rhodium, the author was unable to find any difference in the decomposition voltage (compare Blackadder, A., 1913, ii, 36). J. F. S.

Theory of Heterogeneous Catalysis. L. G. GURVITSCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 837—856).—Detailed investigation of the reaction of pinene with floridin (A., 1915, i, 933) leads to the conclusion that the initial products of this reaction are polyterpenes, which, under the influence of the heat developed, subsequently undergo partial decomposition into simple terpenes. The formation of the polyterpenes is caused by the adsorption of the pinene on the surface of the floridin, propinquity of the pinene molecules being thus effected; factors which impede this adsorption also retard the transformation of the pinene.

A catalytic reaction of another type has been discovered in the action on carbon disulphide of the partly dehydrated aluminium hydroxide obtained from metallic aluminium in presence of traces of mercury; this reaction, which proceeds at the ordinary temperature, is expressed by the equation $CS_2 + 2H_2O = 2H_2S + CO_2$. The yield of hydrogen sulphide attains a maximum for a certain percentage of water in the alumina, and the conclusion is drawn that the transformation of the carbon disulphide is a result of its adsorption, that is, of the approach of the carbon disulphide molecules to the water molecules within the sphere of action of the molecules of alumina. In a similar manner, alumina prepared as described above causes the conversion of ethyl chloride into ethyl alcohol in the cold.

The hypothesis that adsorption always forms the basis of heterogeneous catalysis also furnishes a very simple explanation of those reactions in which the formation of intermediate chemical compounds is usually assumed, for instance, the reactions of Ipatiev, Sabatier, Bredig, etc. T. H. P.

A Laboratory Gas Meter. E. G. BECKETT (*J. Soc. Chem. Ind.*, 1917, **36**, 52).—The apparatus consists essentially of a glass **U**-tube, the limbs of which are connected by a glass siphon, as shown in the annexed diagram. It is filled up to the dotted line *AB* with water (or other suitable mobile liquid), which thus fills the siphon, *C*. When the gas to be measured enters the apparatus, it forces the level of the water down in *A* and up in *B* until the difference in pressure causes the siphon to empty itself into *B*. The gas in *A* then escapes into *B* through the siphon, whilst the level of the water readjusts itself in the **U**-tube and the siphon again becomes filled. The process then starts again. The siphon runs over each time after a definite amount of gas has passed through the instrument, which amount, however, varies with the velocity of the gas.



The apparatus has the advantage that it can be used for corrosive gases, such as chlorine, for which the ordinary metallic gas-meter is quite unsuitable.

If a constant stream is desired, gas at a high pressure should be employed and the rate regulated or throttled immediately in front of the meter. H. W.

Inorganic Chemistry.

The Absolute Density of Hydrogen Bromide Gas. C. K. Reiman (*Compt. rend.*, 1917, **164**, 44—46).—Using the direct weighing method described by Moles (A., 1916, ii, 314, 526), determinations have been made of the weight of a normal litre of hydrogen bromide, the gas having been prepared either by the direct combination of hydrogen and bromine or by the action of syrupy phosphoric acid on potassium bromide, the resultant gas being purified in each case by fractional distillation of the liquefied gas. The value obtained, as a result of thirty-one determinations, for the weight of a normal litre of the gas is $3{\cdot}6442 \pm 0{\cdot}0002$ grams.

W. G.

Electrolytic Oxidation of Sulphurous Acid. M. de K. Thompson and N. J. Thompson (*Met. and Chem. Eng.*, 1916, **15**, 677—679; from *J. Soc. Chem. Ind.*, 1917, **36**, 81).—The apparatus consisted of an earthenware cup as diaphragm containing a cylindrical nickel cathode with a cylindrical platinum gauze anode surrounding the diaphragm, the porous cup being filled either with sulphuric acid or sodium sulphite. The anodic compartment con-

tained a solution of sulphur dioxide (1—5%); during electrolysis, the anode solution was kept saturated by passing in a current of sulphur dioxide. The current density was about 0·0075 ampere per sq. cm. Results proved that sulphurous acid is easily oxidised at platinum anodes to sulphuric acid of any concentration below 95%. The concentration of sulphuric acid in the cell has a great effect on the current efficiency, as also, but in a less degree, has the current density. Oxidation occurs with high current efficiencies even in concentrated sulphuric acid solutions. For a given concentration of sulphuric acid, the current efficiency decreases with increasing current density. H. W.

Catalytic Oxidation of Ammonia. E. BUCH ANDERSEN (*Zeitsch. Elektrochem.*, 1916, **22**, 441—443).—The oxidation of ammonia to nitric oxide and nitrogen dioxide has been investigated with regard to the connexion between the yield of oxide and the temperature and the rate of passage of the gas over the catalyst. It is shown that the yield of oxide is dependent on the temperature, but in the presence of the slightest excess of oxygen it is practically quantitative. Thus, varying the ammonia concentration from 2·5 to 5 volumes per cent., the temperature from 500° to 1000°, and the time of contact with the catalyst from 1·15 secs. to 0·18 sec., the author has been unable to detect any change in the amount of nitrogen dioxide produced. The amount of oxide produced depends mainly on the use of a catalyst which, whilst accelerating the oxidation, does not affect the decomposition of the oxide. It is stated that by use of a suitable catalyst it is possible at 500° to obtain a rapid and complete oxidation of ammonia, provided that the amount of ammonia does not exceed the amount corresponding with the oxygen admitted. J. F. S.

Preparation of Carbonyl Chloride. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 457—458).—The catalytic effect of salts is often explainable by the formation of complexes containing the catalyst and the substances reacting under its influence. Such complexes then undergo decomposition, which is induced either by temperature conditions or by the presence of compounds causing a diminution of the stability of the complexes. In this connexion interest attaches to the compounds of aluminium chloride with carbonyl chloride obtained by Baud (A., 1905, ii, 525).

[With SALATKO-PETRISCHTSCHE.]—Carbonyl chloride is formed when carbon monoxide and chlorite are passed through a tube containing pieces of aluminium chloride at 30—35°, or, still better, if the gaseous mixture is passed through a saturated solution of aluminium chloride in chloroform; subsequent treatment of the chloroform solution with water yields a considerable quantity of carbon dioxide. T. H. P.

Borates: The System $Na_2O:B_2O_3:H_2O$ at 60°. III. U. SBORGI and F. MECACCI (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 455—458).—The complete diagram for this system at 60° is now

given. The results show that the solubility of sodium oxide is 97·04 parts per 100 parts of water at 100°, this value being in accord with that usually accepted. Of the compounds formed at 60°, the 1 : 1 : 1 and the 2 : 1 : 1 ($Na_2O : B_2O_3 : H_2O$) compounds have not previously been described. T. H. P.

Preparation of Sodium Perborate. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT VORM. ROESSLER (Brit. Pat., 100153, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 83).—A solution containing a carbonate (13—15% anhydrous) and an alkali borate is electrolysed, the borate reacting with the percarbonate formed to produce perborate. It is essential that the solution should be kept saturated with borax, and that solid perborate be always present; it is advisable that catalysts should be absent. This may be effected by using pure substances or by adding materials such as alkali hydrogen carbonate, stannic acid, or magnesium silicate (1—2 grams per litre of electrolyte). H. W.

Preparation of Alkali Perborates. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT VORM. ROESSLER (Brit. Pat., 102359, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 83).—Sodium perborate is made by electrolysing lyes containing soda and borax. The accumulation of sodium hydrogen carbonate, produced during the action, must be restricted to a maximum of 70—75 grams per litre; otherwise the stability of the perborate is adversely affected. Hence, metaborate or free alkali and borax are added during the electrolysis; or lime, or other alkali, is added to the waste lye prior to its treatment or re-treatment. H. W.

The Double Salts of Cæsium Chloride with Calcium and Strontium Chlorides. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1917, [iv], **43**, 67—68).—The double salt, $2CsCl,CaCl_2,2H_2O$, crystallises from solutions which contain very variable proportions of the two chlorides. The molar ratio may, in fact, be varied from $CsCl/CaCl_2 = 4$ to 0·25.

Solutions containing cæsium chloride and strontium chloride in the molar ratio 2 : 1 deposit crystals of the double salt,

$$5CsCl,2SrCl_2,8H_2O.$$

Cæsium chloride does not form a double salt with barium chloride. H. M. D.

Metallographic Study of the System Silver–Tellurium. MASUMI CHIKASHIGE and ISABURO SAITO (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 361—368. Compare Pélabon, A., 1906, ii, 667; Pellini and Quercigh, A., 1910, ii, 1063).—Two compounds are formed, of which one, Ag_2Te, melts sharply at 957°, whilst the other, to which the formula Ag_7Te_4 is assigned, decomposes below its melting point, and exists in two modifications, each of which corresponds with a short branch of the freezing-point curve. β-Ag_7Te_4 is formed from Ag_2Te and liquid at 443°, and changes into the α-modification at 403°. Solid solutions are not formed. Eutectics occur at 32%

Ag and 350°, and at 87·5% Ag and 870° respectively. Annealing experiments indicate that the transformation is one of a single compound, and that a second compound, such as Ag_3Te_2, is not formed. C. H. D.

Alloys of Certain Haloid Salts of Silver and of Alkali Metals. S. F. SHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 203—221. Compare A., 1907, ii, 258).—The systems NaBr–AgBr, NaCl–AgCl, and KBr–AgBr have been studied thermally and micrographically.

With NaBr–AgBr, results in accord with those of Sandonnini and Scarpa (A., 1914, ii, 204) have been obtained. The character of the cooling curves indicates the formation of an uninterrupted series of solid solutions, and the melting-point diagram corresponds with type I of Roozeboom's classification. The cooling curves, however, have not quite the simple form of those of solid solutions, but exhibit certain anomalies, depending on the generation of heat, almost at the completion of the solidification. The explanation of this phenomenon is as follows: Owing to the low velocity of diffusion, the crystals of the solid solution which separate first and are richer in sodium bromide do not absorb the amount of silver bromide required by the conditions of equilibrium at the given temperatures; in consequence of this, there remains an excess of almost pure silver bromide, which finally crystallises, and gives rise to a new halt on the cooling curve.

The melting-point results for the system NaCl–AgCl are almost identical with those obtained by Botta (A., 1911, ii, 293) and by Sandonnini (A., 1911, ii, 800), except that the melting points of sodium and silver chlorides are found to be 816° and 451° respectively. Both silver bromide and chloride exhibit changes of colour with change of temperature.

The results obtained with the system KBr–AgBr agree with those of Sandonnini (A., 1912, ii, 941), with the exception that the composition at the eutectic point, 285°, corresponds with 67 mol. % of silver bromide, and not with 56 mol. %.

Sections formed by the solidification of the mixtures between the microscope slide and cover-glass were examined in reflected light, both ordinary and polarised. The alloys of silver and sodium bromides exhibit structures similar to those of metallic solid solutions, the crystals being polyhedral and bordered by more or less thin lines, and, especially in the thicker sections, having a zonal structure resulting from the inadequate velocity of diffusion mentioned above. Similar appearances are observed with the system AgCl–NaCl. Sections containing more than 75 mol. % of sodium bromide or 60 mol. % of sodium chloride could not be prepared owing to the softening of the glass at the high temperatures required, but up to these limits the alloys are anisotropic. The structures of these sections and of those of the system AgBr–KBr are in complete correspondence with the melting-point diagrams.

T. H. P.

Lead Subiodide and an Improved Method for Preparing Lead Suboxide. The Solubility of Lead Iodide. HENRY GEORGE DENHAM (T., 1917, **111**, 29—41. Compare Denham and Allmand, T., 1908, **93**, 424).—In the earlier paper it has been shown that, in the presence of platinised platinum, hydrogen can reduce bivalent salts of lead to a lower state of valency. The treatment of lead suboxide with an acid or of a solution of a lead salt with metallic lead fails to produce lead sub-salts. However, by the action of methyl iodide vapour on a mixture of lead suboxide with four times its weight of silica at 260° in an atmosphere of nitrogen, it is possible to obtain lead subiodide, PbI (compare Denham, A., 1911, ii, 804), as a bright yellow solid, which on heating decomposes above 300°, with formation of lead iodide and metallic lead, a similar decomposition being effected by the action of acids. Lead subiodide appears to undergo slow oxidation in the air; it is much less soluble in water than is lead iodide, the solubility ratio, judged from the relative electrical conductivity of the two salts measured in a special apparatus, being approximately 1:9; the solution gives no trace of a precipitate with potassium chromate or hydrogen sulphide.

A determination of the solubility of ordinary lead iodide in water, based on the electrical conductivity of a saturated aqueous solution at 25° in a vacuum, and assuming complete dissociation, gave a result in exact agreement with that of von Ende (A., 1901, ii, 241; see also Lichty, A., 1903, ii, 480; Böttger, A., 1904, ii, 241).

The lead suboxide necessary for the above preparation of lead subiodide was obtained by the decomposition of lead oxalate at 270—335°, with continuous removal of the gaseous products by a mercury pump (compare Tanatar, A., 1901, ii, 451; Glaser, A., 1903, ii, 646; Brislee, T., 1908, **93**, 154). The product is a dark powder, which at 375° becomes paler in colour and somewhat less reactive towards methyl iodide, although its composition is unaltered.

For experimental details, see the original paper. D. F. T.

Reduction of Lead Sulphate. G. A. PERLEY and C. W. DAVIS (*J. Physical Chem.*, 1916, **20**, 151—163).—Whilst studying methods of regenerating sulphated accumulator plates, the authors noticed that when sodium hydroxide, lead, and lead sulphate were in contact simultaneously, crystals of lead were deposited. This reaction has been carefully studied in the present paper. It is shown that pure lead dissolves slowly in pure sodium hydroxide solution, but experiments under reduced pressure and in the absence of air failed to show any appreciable evolution of gas. The formation of lead crystals when lead, lead sulphate, and sodium hydroxide are in contact, is not dependent on impurities in the lead. All three substances are necessary, and the crystals are not obtained by the action of sodium hydroxide on lead or on lead sulphate. While the lead crystals are forming, the lead plate is being corroded,

and the net result is a decrease in the total amount of metallic lead. The formation of lead crystals in alkaline solution is not due to fluctuations of temperature, with the intermediate formation and decomposition of a lead salt with a lower valency, although this is what happens in Denham's experiments with lead and lead acetate (T., 1908, **93**, 424). The rapid formation of fine lead crystals is due to a concentration cell consisting, in principle, of $Pb|NaOH|Na_2SO_4,PbSO_4|Pb$. The sodium hydroxide dissolves the lead sulphate, and the denser solution thus formed flows to the bottom of the container, while fresh sodium hydroxide flows in from above to replace it, thus setting up concentration differences. It is necessary to assume that the conversion of lead ions into plumbite ions takes time, and that the amount of lead sulphate dissolved as such is greater than it should be until equilibrium is reached. Rotating a sulphated lead strip makes the reduction more rapid and more uniform. This is not an argument against the reaction being due to a concentration cell. Rotating the electrode increases the removal of plumbite solution from the projecting portions of the electrode, but has less effect on the sunken portions, where there is more lead sulphate. We thus have the paradox that stirring increases the concentration differences, causing more rapid and more uniform reduction. On long keeping, large crystals of lead are formed at the lower edge of the sulphated plate. These continue to grow after all the lead sulphate has disappeared. These crystals are due to the action of a concentration cell consisting, in principle, of $Pb|\text{dil. }Na_2PbO_2|\text{conc. }Na_2PbO_2|Pb$. This can be duplicated by placing a lead strip in a test-tube, pouring in a concentrated solution of sodium hydroxide, and superposing a solution of lead sulphate in more dilute sodium hydroxide. Beautiful crystals of lead are then formed in the upper portion of the tube. J. F. S.

Iron Trisulphide and the Formation of Amorphous Iron Disulphide. V. Rodt (*Zeitsch. angew. Chem.*, 1916, **29**, i, 422—423).—There being much uncertainty regarding the existence of iron trisulphide, the author has further investigated the subject, with the following results. When moist ferric hydroxide, or ferric hydroxide suspended in water, is treated with hydrogen sulphide, it becomes black, owing to the formation of ferric trisulphide, in accordance with the equation $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 3H_2O$. In a moist condition in the absence of air, or in the presence of excess of hydrogen sulphide, it is transformed into a mixture of the disulphide and sulphide, thus: $Fe_2S_3 = FeS_2 + FeS$. This transformation takes about a week at the ordinary temperature, but only a few hours at 60°. The mixture thus produced is only partly soluble in dilute hydrochloric acid, whereas the trisulphide is readily and completely soluble. The transformation is prevented, in the absence of air, by small quantities of alkali, and even magnesium carbonate and calcium carbonate have a retarding

effect. When dried in a vacuum over phosphoric oxide, iron trisulphide is very stable.

When exposed to the action of the air in the presence of alkaline substances, ferric trisulphide gradually becomes light yellow in colour, sulphur being deposited. The product resembles limonite in appearance, and when dried gives a fine, yellow powder containing a constant percentage of water, which is less than that corresponding with ferric hydroxide.

The above results are used to explain the various discrepancies found in the literature with respect to ferric trisulphide.

Feld's statement that iron disulphide is formed when precipitated ferrous sulphide is boiled with flowers of sulphur is confirmed; even ordinary ferrous sulphide, if finely powdered, and finely powdered crystalline sulphur, act in the same way. Iron disulphide is also formed when a solution of sodium trisulphide is added slowly to a boiling solution of ferrous sulphate, sulphur being liberated at the same time. Care must be taken that at no time is the sodium trisulphide in excess, otherwise the formation of iron disulphide is prevented.

Bischof's observations on the production of iron pyrites in nature ("Lehrb. chem. physik. Geologie," I, 357, 917) are in complete agreement with the fact that the final product of the action of hydrogen sulphide on ferric hydroxide in the absence of alkaline substances is iron disulphide. T. S. P.

Metallographic Study of the System Antimony Sulphide–Cuprous Sulphide. MASUMI CHIKASHIGE and YOSHINDO YAMAUCHI (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 341—347. Compare Pélabon, A., 1905, ii, 435; Parravano and de Cesaris, A., 1912, ii, 942).—The sulphides are fused together in Jena-glass or porcelain tubes in nitrogen. The freezing-point curve has two maxima, corresponding with $4Cu_2S,5Sb_2S_3$, melting at about 520°, and $3Cu_2S,Sb_2S_3$, melting at 571°. There are eutectic points at 7%, 37%, and 68% of cuprous sulphide, the eutectic temperatures being 463°, 514°, and 562° respectively. Solid solutions are not formed. The microscopical examination confirms the thermal results. It has not been determined whether the native mineral chalcostibite, usually regarded as the metathioantimonite, has the formula Cu_2S,Sb_2S_3 or $4Cu_2S,5Sb_2S_3$. The second compound described above may be regarded as cuprous orthothioantimonite. C. H. D.

The Probable Movement of Atoms in Bismuth during Crystal Gliding. A. JOHNSEN (*Centr. Min.*, 1916, 385—392).—The existence of two sets of gliding-planes in rhombohedral crystals of bismuth, considered in connexion with the structure of the point-system and *X*-ray analysis, indicates that the molecules are diatomic and that these possess the same degree of symmetry as the whole crystal. The atomic centres are $3\cdot10^{-8}$ cm. apart. This agrees with the facts that bismuth dissolved in a large quantity of lead is diatomic, and that the vapour density of bismuth at 1600—1700° lies between that for Bi and Bi_2. L. J. S.

The Melting Point of Palladium and Wien's Constant C_2. G. HOLST and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 549—550).—The constant c_2 in Wien's radiation formula, $\lambda \log E_1/E_2 = c_2(1/T_2 - 1/T_1)$, in which E_1 and E_2 are the emissive powers of the black body at the melting points of palladium (T_1) and gold (T_2) respectively, is for $\lambda = 0{\cdot}6563\,\mu$ equal to 14465 ± 5 if the melting point of palladium is taken as 1549°. If in accordance with the scale of the Physikalische Technische Reichsanstalt $c_2 = 14300$, the formula gives 1557° as the melting point.

H. M. D.

Mineralogical Chemistry.

Occurrence of Silver in Argentiferous Galena Ores. ARVID E. NISSEN and SAMUEL L. HOYT (*Economic Geology*, 1915, **10**, 172—179).—In order to determine the state in which silver exists in argentiferous galena, fusions of lead and silver sulphides were examined. The following conclusions are drawn: (1) Silver occurs as argentite in some primary and in some secondary argentiferous galena ores. (2) The limit of solid solution at atmospheric temperatures is below 0·2% Ag_2S. (3) The eutectic, as given by Friedrich (1907), is not developed in concentrations below 2·70% Ag_2S. L. J. S.

Minium from Biberwier, Tyrol. E. DITTLER (*Centr. Min.*, 1916, 521).—This occurs as an alteration product of galena, the red nodules still containing a nucleus of galena. Analysis (Pb, 80·60; S, 6·33; gangue, 8·29 = 95·22%) proves the presence of galena 47·17, with minium (Pb_3O_4) 43·81%. The alteration has been effected by weathering, probably with a basic carbonate as an intermediate stage. L. J. S.

The Refractive Indices of Rhombohedral Carbonates. PAUL GAUBERT (*Compt. rend.*, 1917, **164**, 46—49).—Determinations of the refractive indices have been made on a number of mineral carbonates, the values obtained being as follows: for giobertite, $\epsilon = 1·5148—1·5170$, $\omega = 1·7053—1·7115$; for siderite, $\epsilon = 1·5982—1·6020$, $\omega = 1·7959—1·8120$; for dialogite, $\epsilon = 1·5934—1·6053$, $\omega = 1·8100—1·8194$; for a cupriferous smithsonite, $\epsilon = 1·612$, $\omega = 1·782$; for dolomite, $\epsilon = 1·5021—1·5133$, $\omega = 1·6808—1·6946$; for ankerite, $\epsilon = 1·5148—1·5273$, $\omega = 1·7046—1·7172$; for mesitite, $\epsilon = 1·5873$, $\omega = 1·7632$. The values calculated from the chemical composition, using the laws governing the relations between the indices of an isomorphous mixture, agree often only approximately with those found, this being due to the fact that specimens from the same locality often show slight variations in composition. The author has found that the refractive indices may vary even in the same crystal, owing to zone structure in the crystal. W. G.

Dahllite from Kangerdluarsuk, Greenland. O. B. BÖGGILD (*Jahrb. Min.*, 1916, ii, Ref. 163—165; from *Meddelelser om Grönland*, 1915, **51**, 434—443).—The rock naujaite occurring at Kangerdluarsuk and other localities in the neighbourhood of the Tunugdliarfik-Fjord, in south Greenland, contains in crevices crusts of natrolite and dahllite. The latter forms small, hexagonal plates ($n=1\cdot623$—$1\cdot627$, $\omega-\epsilon=0\cdot011$), agate-like, banded masses ($\epsilon=1\cdot591$—$1\cdot607$, $\omega=1\cdot604$—$1\cdot626$, $\omega-\epsilon=0\cdot012$—$0\cdot017$; D 3·000—3·012 and 3·090—3·094), and layers of amorphous material ($n=1\cdot605$—$1\cdot619$). These optical determinations, although varying widely, differ from the constants for apatite. Analysis by C. CHRISTENSEN of the agate-like variety gave the following results, with the ratio $CaO:P_2O_5=4:1$, thus differing from the apatite ratio and also somewhat, from the Norwegian dahllite.

P_2O_5.	CaO.	Al_2O_3.	Na_2O.	CO_2.	H_2O.	Total.
32·40	54·10	3·15*	0·77	8·26	1·32	100·00

* Including: FeO, 0·79; K_2O, 0·11.

A study of the optical constants and specific gravity as functions of the chemical composition of the phosphorite minerals leads to no definite result, but these minerals are to be regarded as distinct from apatite. L. J. S.

New Phosphates from Greifenstein, Saxony. F. SLAVÍK (*Jahrb. Min.*, 1916, ii, Ref. 31—34; *Abh. böhm. Akad.*, 1914, No. 4, 19 pp.).—*Ježekite*, at first erroneously referred to as "epistilbite," forms colourless to white monoclinic prisms, needles, and plates, $a:b:c=0\cdot8959:1:1\cdot0241$; $\beta=105°31\frac{1}{2}'$. Cleavage (100) perfect. $H=4\frac{1}{2}$; $D=2\cdot940$; refractive indices, $\alpha=1\cdot55$, $\beta=1\cdot56$, $\gamma=1\cdot59$. Analysis I, by E. SKARNITZL, gives the formula $P_2O_5,Al_2O_3,CaO,2NaF,2NaOH$ or $(PO_4)_2F_2(OH)_2Al(AlO)CaNa_4$.

Roscherite, a new mineral of the childrenite group, forms dark brown columns or plates. Monoclinic, $a:b:c=0\cdot94:1:0\cdot88$; $\beta=99°50'$; cleavage (001) and (010) good. $H=4\frac{1}{2}$; $D=2\cdot916$; $n=1\cdot625$—$1\cdot63$. Analysis II, by K. PREIS, gives the formula $(Mn,Fe,Ca)_2Al(OH)P_2O_8,2H_2O$.

Lacroixite, at first mistaken for "herderite," is pale yellow or green and indistinctly crystallised; probably monoclinic and pseudo-rhombic ($a:b:c=0\cdot82:1:1\cdot60$). $H=4\frac{1}{2}$; D 3·126; $n=1\cdot57$. Analysis III, by A. JILEK, gives $Na_4(Ca,Mn)_4Al_3P_3O_{16}(F,OH)_4,2H_2O$, or nearly $2NaR''(AlO)PO_4F,H_2O$.

	P_2O_5.	Al_2O_3.	FeO.	MnO.	CaO.	Na.	Li.	F.	H_2O.	Total.
I.	30·30	21·92	—	trace	13·50	18·71	0·86	8·15	—	100·70*
II.	35·98	13·01	9·58	13·70	10·87	trace	—	—	11·52	99·24†
III.	28·92	18·92	—	8·45	19·51	—	—	—	4·22	100·00‡

* Including. OH, 7·26; Fe_2O_3, trace. † Including: insoluble residue 4·58%.
‡ Including: NaF, 14·47; NaOH, 5·51%.

L. J. S.

Crandallite, a New Mineral. G. F. LOUGHLIN and W. T. SCHALLER (*Amer. J. Sci.*, 1917, [iv], **43**, 69—74).—This new hydrated phosphate of calcium and aluminium is found as compact to cleavable masses filling irregularly shaped cavities in a quartz-barytes gangue with pyrites, enargite, etc., in the Brooklyn mine, Silver City, Tintic District, Utah. It is white to grey with shades of yellow or brown. Under the microscope the cleavage plates are seen to be composed of fine radiating fibres, and it is probable that the cleavages represent a pre-existing mineral (goyazite?), the alteration of which has given rise to the fibrous crandallite. In addition to this, the material is much confused by the presence of large amounts of impurities in fine dissemination. The mineral is soluble in acids. Analysis by W. T. SCHALLER gave, after deducting 35·13% soluble:

Al_2O_3.	CaO.	SrO.	MgO.	P_2O_5.	SO_3.	H_2O at 105°.	H_2O >105°.	Total.
38·71	7·50	2·21	0·94	27·09	3·80	1·29	18·86	100·40

This gives the formula $CaO,2Al_2O_3,P_2O_5,5H_2O$, with slight replacement of CaO by SrO and MgO, and of P_2O_5 by SO_3, or, more exactly, of $(HPO_4)''$ by $(SO_4)''$, conforming with the type of the gorceixite formula $(BaO,2Al_2O_3,P_2O_5,5H_2O)$, and differing slightly from that of goyazite $(2SrO,3Al_2O_3,2P_2O_5,7H_2O)$. It is suggested that crandallite and gorceixite belong to a group of fibrous minerals which have been produced by the alteration of minerals of the closely allied alunite–beudantite group. L. J. S.

Natrojarosite from Kundip, Western Australia. EDWARD S. SIMPSON and MAURICE A. BROWN (*J. Roy. Soc. Western Australia*, 1916, **1** (for 1914–1915), 45—54).—Dull, porous, ochre-yellow masses of natrojarosite occur in oxidised gold ore on the Harbour View mineral lease at Kundip in the Phillips River gold-field. Under the microscope, the material is seen to be minutely crystalline in rhombohedral scales. Analysis agrees closely with the formula $Na_2O,3Fe_2O_3,4SO_3,6H_2O$ or $Na_2[Fe(OH)_2]_6(SO_4)_4$. The material is only slowly attacked by hot concentrated nitric acid, but is dissolved by hot concentrated hydrochloric acid, and it is readily decomposed by a hot solution of sodium hydroxide. There is no loss at 150°; at a red heat all the water and three-quarters of the sulphuric anhydride are expelled. The mineral has probably been formed by the weathering of pyritous ore in the presence of sodium-bearing rocks and ground waters.

Na_2O.	K_2O.	Fe_2O_3.	FeO.	SO_3.	P_2O_5.	H_2O.	Total.	Sp. gr.
6·32	0·68	49·86	0·16	32·30	0·20	10·93	100·45	3·11

L. J. S.

Composition of Thaumasite from Great Notch, New Jersey. GLENN V. BROWN (*Amer. Mineralogist*, 1916, **1**, 81).—Analysis of material from a 100-lb. mass of thaumasite, found about 1908 in the basalt of the Francisco quarry at Great Notch,

gave the following results, agreeing closely with the formula $CaCO_3,CaSiO_3,CaSO_4,15H_2O$.

CaO.	MgO.	$(Al,Fe)_2O_3$.	CO_2.	SiO_2.	SO_3.	H_2O (below 100°).	H_2O (above 100°).	Total.
27·18	0·02	0·20	7·97	9·36	13·03	0·32	42·24	100·31

L. J. S.

The System Anorthite–Forsterite–Silica. H. E. Boeke (*Centr. Min.*, 1916, 313—317).—A criticism and discussion of Andersen's paper (A., 1915, ii, 361). The quaternary system $CaO–MgO–Al_2O_3–SiO_2$ may be represented by means of a regular tetrahedron with these components placed at the four corners. Besides the compounds forsterite ($2MgO,SiO_2$), clinoenstatite (MgO,SiO_2), diopside ($MgO,CaO,2SiO_2$), anorthite ($CaO,Al_2O_3,2SiO_2$), and spinel (MgO,Al_2O_3), there is a possibility of others, namely, calcium silicates ($CaSiO_3$, $Ca_3Si_2O_7$, Ca_2SiO_4, Ca_3SiO_5), gehlenite ($2CaO,Al_2O_3,SiO_2$), sillimanite (Al_2O_3,SiO_2), cordierite ($2MgO,2Al_2O_3,5SiO_2$), and garnet ($3[Ca,Mg]O,Al_2O_3,3SiO_2$). L. J. S.

Natural and Artificial Ultramarine. C. Doelter (*Jahrb. Min.*, 1916, ii, Ref. 24; from *Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. I, 1915, **124**, 37—48).—As opposed to Brögger and Bäckström (1890), who regarded ultramarine, lazulite, haüyne, and sodalite as atomic compounds, these are considered to be molecular compounds of the nephelite silicate, $NaAlSiO_4$, with NaCl, Na_2SO_4, Na_2S, NaS, NaS_2, etc. The coloration of ultramarine appears to depend on the presence of free colloidal sulphur or polysulphides; in white ultramarine these are not present, only Na_2S. Support to this view is given by the action of radium emanations on ultramarine of various colours. L. J. S.

Leifite, a New Mineral from Narsarsuk, Greenland. O. B. Böggild (*Jahrb. Min.*, 1916, ii, Ref. 161—162; from *Meddelelser om Grönland*, 1915, **51**, 427—433).—The new mineral occurs with felspar, aegirite, and zinnwaldite in the drusy pegmatite veins at Narsarsuk, near Julianehaab. It is colourless to white, with a faint violet sheen, and has the form of hexagonal prisms, without terminal faces, reaching to 2 cm. in length and 5 mm. in thickness. There is a perfect cleavage parallel to the prism faces and a conchoidal cross-fracture. $H=6$, $D=2·565—2·578$. Optically uniaxial and positive, $\epsilon=1·5224$, $\omega=1·5177$. The mineral is not decomposed by hydrochloric acid. It fuses extremely easily, with intumescence, to a colourless glass. Analysis by C. Christensen gave:

SiO_2.	Al_2O_3.	MnO.	Na_2O.	F.	H_2O.	Total (less O for F).
67·55	12·69	0·41	15·47	4·93	0·77	99·74

This gives the formula $Na_2Al_2Si_9O_{22},2NaF$ or $Na_4(AlF)_2Si_9O_{22}$

The degree of acidity is greater than in the acid silicates, petalite, and milarite, and is exceeded only in the Greenland minerals neptunite, narsarsukite, and lorenzenite. L. J. S.

An American Occurrence of Miloschite. EDGAR T. WHERRY and GLENN V. BROWN (*Amer. Mineralogist*, 1916, **1**, 63—67).—A blue, earthy mineral found in a gossany vein near Ely, Nevada, resembling chrysocolla in appearance, but containing no copper, is identified with the Serbian miloschite. The optical characters of the minute, crystalline grains suggest monoclinic symmetry; refractive indices, $\alpha = \beta = 1{\cdot}552$, $\gamma = 1{\cdot}559$. The following mean of two analyses by G. V. BROWN gives the kaolinite ratios $H_4R'''_2Si_2O_9$. The mineral may thus be regarded as a chromiferous kaolinite, corresponding with fuchsite, the chromiferous variety of muscovite, from which it has no doubt been derived.

SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	H_2O at 105°.	H_2O at 300°.	Total.
43·47	34·41	3·85	0·86	0·37	0·12	0·28	3·54	13·27	100·17

L. J. S.

Mineralogical Notes. ESPER S. LARSEN and GEORGE STEIGER (*J. Washington Acad. Sci.*, 1917, **7**, 6—12).—Aphrosiderite from British Columbia.—A fossiliferous slate of Cambrian age occurring near Field, in British Columbia, carries numerous veinlets of pale green chlorite with some pyrites and calcite, the veinlets being roughly parallel to one another and perpendicular to the cleavage of the slate. The slate is very fine in texture, and is made up largely of muscovite, with some kaolinite and very little quartz, apatite, and pyrites: analysis I. The chlorite has H 1—2, D 2·959, *n* 1·625, and is almost isotropic; anal. II is near

$$5(Fe,Mg)O,2Al_2O_3,4SiO_2,5H_2O,$$

which lies between the formulæ usually assigned to aphrosiderite and delessite.

Thuringite from Colorado.—This occurs in large amount as a primary filling in the metalliferous veins cutting rhyolite near Creede. It is green, soft and friable, and fibrous to platy in structure. Material from different mines shows variations in the refractive indices (*n* 1·585—1·643), suggesting variations in chemical composition. Anal. III of material from the Last Chance mine on the Amethyst vein.

Griffithite, a new member of the chlorite group.—This occurs as a filling in amygdaloidal cavities in basalt at Cahuenga Pass, Griffith Park, Los Angeles, California. It differs both optically and chemically from any chlorite previously described. It is dark green, H about 1, D 2·309; fusible at 4, with intumescence to a black, magnetic slag; and gelatinised by hydrochloric acid. It is optically negative, with the first mean line normal to the perfect basal cleavage, $2V = 0°—40°$, $\alpha = 1{\cdot}485$, $\beta = 1{\cdot}569$, $\gamma = 1{\cdot}572$; pleo-

chroism, pale yellow to brownish-green. Analysis IV gives the formula $4(Mg,Fe,Ca)O,(Al,Fe)_2O_3,5SiO_2,7H_2O$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
I.	54·49	25·60	0·89	2·00	1·18	1·90	0·28	6·67
II.	24·97	23·76	1·55	26·86	10·81	trace	0·26	0·97
III.	24·34	16·46	12·04	28·89	5·41	nil	0·37	trace
IV.	39·64	9·05	7·32	7·83	15·80	2·93	0·71	nil

	H_2O at 105°.	H_2O >105°.	TiO_2.	Total.
I.	0·33	3·91	0·72	99·83*
II.	10·71		0·11	100·00
III.	0·35	9·19	trace	99·80†
IV.	12·31	4·90	nil	100·49

*Including: CO_2, 1·54; P_2O_5, 0·08; S, 0·24; CuO, trace. † Including: MnO, 2·75; CO_2, P_2O_5, S, traces.

L. J. S.

Minerals from the Manganese Ore Deposits of Oberhalbstein, Grisons, Switzerland. F. P. Müller (*Centr. Min.*, 1916, 457—459).—Small, lenticular masses of oxidised manganese ore occur in schistose rocks associated with serpentine at this locality. The minerals present include zoisite, epidote, piedmontite, rhodochrosite, rhodonite, and a hydrous manganese silicate. The last is reddish-brown, with a metallic lustre. H=3½, D slightly less than that of quartz (2·65), n 1·54—1·55, birefringence 0·025—0·027; optically negative and usually uniaxial. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	CuO.	Na_2O.	K_2O.	H_2O.	Total.
47·15	5·09	0·36	36·89	trace	2·99	trace	0·07	1·21	6·24	100·00

L. J. S.

Titaniferous Augite from Ice River, British Columbia. Charles H. Warren and John A. Allan, with analysis by M. F. Conner (*Amer. J. Sci.*, 1917, [iv], **43**, 75—78).—A black, strongly pleochroic augite is present in the basic (melanocratic) separations from the nephelite-syenite magma of this district, forming at times the greater part of the rock, which then becomes an augitite. It has the form of small grains or prisms, and is remarkable in containing numerous rod-like inclusions arranged parallel to the a- and c-axes of the crystal. These inclusions are black and opaque, and are probably ilmenite. The extinction-angle of the augite on the plane of symmetry is 42·3°. Analysis shows the presence of much titanium dioxide, exceeding any previously recorded (TiO_2 2·85% in augite from a monchiquite from Rio de Janeiro). It is suggested that the ilmenite molecule, $RTiO_3$, may have crystallised out isomorphously with the metasilicate molecule, $RSiO_3$, of the augite, and that, subsequently becoming unstable in that state, it separated out, and is now represented by the inclusions of ilmenite.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	MnO.	H_2O.	Total.	Sp. gr.
41·80	4·84	9·30	5·44	3·30	10·82	22·89	0·10	1·26	99·75	3·39

L. J. S.

Iron Meteorite from Cookeville, Tennessee. GEORGE P. MERRILL (*Proc. U.S. Nat. Museum*, 1916, **51**, 325—326).—A much weathered mass, weighing 2132 grams, was found about three years ago at Cookeville, Putnam County. It shows a very regular and coarse octahedral structure with bands 2—6 mm. wide of kamacite and very thin plates of taenite. Analysis by J. E. WHITFIELD gave:

Fe.	Ni.	Co.	Fe_2O_3.	NiO.	P.	C.	S.	SO_3.	Ignition.	Total.
61·33	6·38	0·37	27·89	1·10	0·17	0·20	0·38	0·09	2·75	100·66

L. J. S.

The Meteoric Irons of Whitfield Co., Georgia. GEORGE P. MERRILL (*Proc. U.S. Nat. Museum*, 1916, **51**, 447—449).—The following new analysis, by J. E. WHITFIELD, is given of the 117-lb. mass found near Dalton, Whitfield Co., which was first described and analysed by C. U. Shephard (A., 1884, 30).

Fe.	Ni.	Co.	Fe_2O_3.	Cu.	Pt.	Ir.	Si.	S.	P.	C.	Total.
91·469	7·575	0·550	0·350	0·016	trace	0·002	0·001	0·025	0·095	0·004	100·087

Although similar in chemical composition to the Whitfield Co. iron described by W. E. Hidden (A., 1882, 153), it differs essentially in structure, as shown on the etched surfaces, and the two irons belong to distinct falls. The Cleveland, Tennessee, iron described by G. F. Kunz in 1887 is also distinct. L. J. S.

Analytical Chemistry.

Estimation of Free and Combined Sulphur in Vulcanised Rubber, and the Rate of Combination of Sulphur with Different Types of Plantation Para Rubber. B. J. EATON and F. W. F. DAY (*J. Soc. Chem. Ind.*, 1917, **36**, 16—20).—The sample is finely divided and extracted for one hundred hours with boiling acetone in a Beadle and Stevens apparatus (A., 1913, ii, 444). The paper packet containing the extracted substance (the weight of the sample taken should be 0·1374 gram) is placed in a small glass tube closed at one end; this is inserted in a combustion tube and the paper and its contents are burnt in a current of oxygen. The gases evolved are collected in receivers containing small quantities of $7N$-sodium hydroxide solution. When the combustion is completed, the contents of the receivers are treated with hydrochloric acid containing bromine, and the resulting sulphuric acid is precipitated as barium sulphate. The "free" sulphur in the acetone solution is estimated by evaporating the solvent and oxidising the residue first by evaporation with nitric acid and bromine and then by fusion with a mixture of sodium and potassium carbonates, potassium nitrate, and potassium chlorate. After the fused

mass has been dissolved in dilute hydrochloric acid, the sulphuric acid is precipitated as barium sulphate. Experiments made with different types of Para rubber showed that the rates at which they combined with sulphur were in accordance with their different rates of cure as determined by their physical properties in the load–stretch curves; the percentage of combined sulphur at the optimum time of cure was practically the same (4—4·5%) for all three types. W. P. S.

Estimation of Small Quantities of Arsenic. PETER KLASON (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 5, 1—16).—The author has investigated fully the Fresenius–von Babo method for the estimation of small quantities of arsenic. In order to obtain known quantities of arsenic, standard solutions of arsenious and arsenic acid were prepared, and aliquot portions of these evaporated to dryness for the purposes of the estimation. When arsenious sulphide was used, it was prepared from a known volume of the above standard solutions by precipitation with thioacetic acid, followed by evaporation to dryness; the residue was then dissolved in a dilute solution (2%) of sodium carbonate, and the solution again evaporated to dryness. For the estimation, the dry residues were mixed with a mixture of 3 parts of sodium carbonate to 1 part of potassium cyanide, and the mixture transferred to a bulb tube, the bulb having a volume of about 3·5 c.c. The bulb was heated by a ring burner, supplied with a 20 cm. high draught-chimney, whilst a stream of carbon dioxide was passed through it. In order to prevent the arsenic subliming back, a piece of thick glass rod was put in the tube behind the bulb; the tube where the arsenic condensed was a capillary In the first experiments, in accordance with the instructions usually given, the carbon dioxide was dried before passing through the tube, but it was found that this was not necessary. In later experiments the gas was simply washed and then passed through a tube containing cotton-wool, before coming to the bulb tube. The capillary tube must be quite clean and free from all traces of grease. When the deposition of arsenic was complete, the capillary tube was cut off and weighed on a micro-balance; it was then heated in an argand burner to expel the arsenic, and again weighed when cool, in order to determine the weight of arsenic.

The results obtained, taking weights of arsenic oxide or sulphide varying between 0·0375 and 1·125 mg., were very variable and far from quantitative, the estimated quantities varying from 42% to 95% of the quantities actually taken. The loss was shown not to be due to arsenic remaining behind as sodium arsenide in the reduction mixture, but to be caused by some of the arsenic vapour being carried away in the stream of carbon dioxide. This was proved by attaching to the capillary of the bulb tube another (straight) tube packed with small bits of porcelain followed with a layer (3 mm.) of asbestos, this tube also ending in a capillary. During the estimation the asbestos layer became more or less dark, owing to the deposition of arsenic. When this arsenic was

driven over into the capillary tube (in a stream of pure hydrogen) and its quantity estimated on the microbalance, the amount found accounted for the low percentages mentioned above. By this means quantitative results could be obtained.

A number of estimations of arsenic by the sodium carbonate–potassium cyanide method, as usually carried out (in Sweden), showed the accuracy to be about 90%.

The reaction which takes place when the above reaction mixture is used cannot be simply the formation of potassium cyanate with the liberation of arsenic, since sodium carbonate is present. Reasons are given in support of the scheme: $5NaAsO_2 = 3NaAsO_3 + As_2 + Na_2O$. The sodium arsenate is then reduced by the potassium cyanide to arsenite, which again gives arsenate and arsenic, and so on to completion. It is further shown that if arsenic is present as a salt of ortho-arsenious or -arsenic acid, as is the case when magnesia is added to the reaction mixture, no reduction takes place. When the arsenic is present as sulphide, reaction takes place according to the equation: $As_2S_3 + 3Na_2CO_3 = As_2O_3 + 3Na_2S + 3CO_2$; reduction then takes place as above, no thiocyanate being formed.

The above method cannot be used when organic matter is present, but can be replaced by the following modification of Berzelius's method. The residues containing arsenic, if the latter is present as sulphide, are evaporated down to dryness with concentrated nitric acid. The residue is then mixed with a mixture of equal parts of sodium carbonate and potassium carbonate and a little mercuric oxide, and the resulting mass put into the bulb tube and heated in a stream of oxygen until it is quite white and mercury is no longer deposited in the capillary. It is then reduced in a stream of hydrogen which has been purified by passing through dilute solutions of silver nitrate and mercuric chloride. The arsenic deposited in the capillary is then weighed as given above. The temperature to which the bulb is heated should be such that the reaction mixture does not fuse. If fusion takes place and magnesia is present, ortho-salts are formed, and these are no longer reduced by hydrogen, as mentioned above. Using quantities of arsenious oxide containing from 0·19 to 0·38 mg. of arsenic, good quantitative results were obtained. T. S. P.

Estimation of Boric Acid by Titration in the Presence of Glycerol. B. H. St. John (*Amer. J. Pharm.*, **89**, 8—10).—Methyl-red is a better indicator than is methyl-orange in the neutralisation of borate solutions previous to the titration of the boric acid in the presence of glycerol and phenolphthalein.

W. P. S.

[Sources of Error in the Analysis of Volatile Substances which are difficult to Burn, and a Method by which Accurate Results can be obtained]. C. J. Enklaar (*Rec trav. chim.*, 1917, **36**, 244—246).—See this vol., i, 112.

Determination of the Free Alkali Hydroxide in Soap. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 411—432). —For the determination of the free alkali hydroxide in soap neither the alcohol method nor the barium chloride method gives results which are accurate or reproducible by different workers. The errors of the alcohol method are due principally to: (1) the capability of colloidal soap in an alcoholic medium to adsorb free alkali, and (2) the sparing solubility in alcohol of the "alkali soap" thus formed and its marked retention of the filtrate. When barium chloride is used, special precautions are necessary to prevent hydrolysis of the soap itself. From the results of experiments made by the author, the following method has been derived.

Of the soap, freshly cut from the middle, *a* grams (about 10) are weighed into a flask of about 400 c.c. capacity fitted with a rubber stopper, and dissolved in 20*a* c.c. of boiling distilled water. To the hot solution are gradually added 2*a* c.c. of neutralised (towards phenolphthalein) barium chloride solution containing 30 grams of the salt to 100 grams of water, the liquid being rotated and boiled for a short time as long as the precipitate does not settle. During the dissolution and boiling, the flask is loosely closed with the stopper. When the precipitate settles, the flask is cooled under the tap and tightly stoppered, the cold liquid being immediately filtered through a rapid filter into a conical flask and the filter washed with cold boiled water. Any precipitate remaining in the original flask is washed with three portions of boiled and cooled water, amounting in all to 10*a* c.c., in the closed flask. The liquid is titrated with decinormal acid in presence of phenolphthalein.

The values thus obtained, which the author terms the "alkali numbers," are characteristic for different types of soap. T. H. P.

Volumetric Estimation of Zinc in Zinc Chloride, Nitrate, and Sulphate. F. W. SJÖSTROM (*Farm. Revy.*, 1916, 489—491; *Zeitsch. angew. Chem.*, 1916, **29**, Ref. 511; from *J. Soc. Chem. Ind.*, 1917, **36**, 82).—If an alkaline solution of zinc chloride, nitrate, or sulphate, of known alkali content, is treated with excess of pure hydrogen peroxide solution, the zinc is precipitated quantitatively as zinc perhydroxide and a certain quantity of alkali is neutralised by the liberated anion. The excess of alkali is titrated and the quantity of zinc calculated, allowance being made for any free acid present in the original zinc solution before being made alkaline. H. W.

Estimation of Nickel in Iron Ores. P. COVITZ (*Met. and Chem. Eng.*, 1916, **15**, 682—683; from *J. Soc. Chem. Ind.*, 1917, **36**, 87).—The following method, using dimethylglyoxime, is accurate and reasonably rapid; it does not require the removal of other elements. One gram of the finely powdered ore (100—120 mesh) is dissolved in nitric acid (*D* 1·42, 10 c.c.) and hydrochloric acid (*D* 1·2, 10 c.c.), these quantities being varied to suit the nature of the ore; sufficient nitric acid must be used to oxidise all reduced metals, particularly ferrous iron. After cooling, sulphuric acid

(*D* 1·84, 10 c.c.) is added, and the solution is evaporated until copious white fumes appear. Nitric acid must be expelled completely, or it will interfere in the later stages. The solution is cooled, treated first with water (30 c.c.), then with hydrochloric acid (2—3 c.c.), heated for ten to fifteen minutes, after which tartaric or citric acid (5 grams) is added. The solution is filtered, the filtrate diluted to 125 c.c., and neutralised with ammonia. If on passing the neutral point the solution is brown, enough citric acid is added to produce a green colour. After the solution has been faintly acidified with hydrochloric acid and heated to 70—85°, the nickel is precipitated by the addition of dimethylglyoxime reagent (20 c.c.; 8 grams of dimethylglyoxime in 1 litre of ethyl alcohol); the solution is stirred constantly and allowed to boil. The precipitate is collected in a weighed Gooch crucible and dried at 110° for forty-five minutes. The dried precipitate contains 20·31% of nickel. H. W.

New Method of Precipitation of Platinum Sulphide, and Analysis of Platinised Asbestos. V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 527—529).—The addition of mercuric chloride to a platinum solution prior to precipitation of the metal as sulphide facilitates the estimation of platinum and allows of accurate results being obtained (compare Gaze, A., 1913, ii, 440), but the bulk of the precipitate is greatly increased and injurious mercury vapour is liberated when the precipitate is ignited.

The incomplete precipitation of platinum sulphide under ordinary conditions depends on the formation of a stable colloidal solution of the sulphide, and the author finds that the hydrosol is converted into the insoluble hydrogel if magnesium chloride is present in the solution. The method employed is as follows.

A weighed quantity of about 5 grams of platinum chloride is dissolved in water in a 250 c.c. flask, the solution being made up to volume and mixed. Twenty-five c.c. of this liquid are diluted to about 200 c.c. in a 250—300 c.c. beaker and then treated with a few drops of hydrochloric acid and about 5 grams of magnesium chloride, either in solution or as crystals, per 100 c.c. of liquid. A rapid current of hydrogen sulphide is then passed through the solution until the latter is saturated, the precipitate adherent to the gas-delivery tube being removed by a piece of filter-paper, and the latter dropped into the liquid, which is then boiled until all odour of hydrogen sulphide has disappeared. The platinum sulphide is washed twice by decantation and several times on the filter with water acidified with one or two drops of hydrochloric acid, the wet filter being then charred in a covered platinum crucible and finally ignited in a blow-pipe flame. This method gives results in very close agreement with those obtained electrolytically.

In the case of platinised asbestos, this is treated on a water-bath with aqua regia, which dissolves the platinum and also sufficient magnesium salts to render the subsequent addition of magnesium chloride superfluous. Ten grams of the asbestos are heated in a large beaker with excess of aqua regia (2 parts of hydrochloric and

1 part of nitric acid) on a water-bath until all the black particles disappear from the asbestos and the liquid assumes an orange-yellow colour. The contents of the beaker are carefully poured into a porcelain funnel, the asbestos, which serves as a filtering medium, being washed until the wash-water becomes free from platinum. The filtrate is made up to a litre in a measuring flask and 100 c.c. of the solution evaporated three times to dryness with hydrochloric acid on a water-bath. The residue is dissolved in 50 c.c. of hot water containing 5 c.c. of hydrochloric acid, and the silica and any fibres of asbestos filtered off. The filtrate is diluted with water to about 250 c.c. and the platinum precipitated as sulphide, the subsequent procedure being as described above. With a particular sample of platinised asbestos, five estimations of the percentage of platinum present gave results varying from 7·72 to 7·75 by the electrolytic method and from 7·75 to 7·77 by the above hydrogen sulphide method. T. H. P.

Microchemical Estimation of Small Quantities of Platinum in the Presence of Gold and Silver. M. VAN BREUKELEVEEN (*Rec. trav. chim.*, 1917, **36**, 285—288).—A rapid method for estimating the amount of platinum in gold- or silver bars. The gold (0·25 gram) is melted with twice its weight of silver, free from platinum, the button being rolled into a thin sheet. This is heated for twenty minutes with 25 c.c. of concentrated sulphuric acid on a sand-bath, the warm acid is decanted, the residue washed with water, and dissolved in the smallest possible quantity of aqua regia. The solution is evaporated to dryness, the residue being further evaporated with a little hydrochloric acid. The final residue is heated at 170—190° for half an hour, the gold being thereby converted into insoluble aurous chloride. To the residue 2 drops (0·1 c.c.) of $N/3$-hydrochloric acid are added, the mixture stirred, and a drop transferred by a loop to a slide and a trace of solid potassium chloride added. After a minute, if platinum is present, yellow octahedra of potassium platinichloride are visible under a microscope. Two more drops of acid are added to the residue, and a second drop removed and examined under the microscope after the addition of potassium chloride. This process is continued until crystals of potassium platinichloride are no longer visible. By working under the same conditions with a gold of known platinum content, it is possible to determine the value of two drops of the $N/3$-hydrochloric acid in terms of platinum percentage in the original alloy. If the alloy under examination is silver with a trace of platinum, then 0·5 gram is used and melted with 0·125 gram of gold free from platinum. W. G.

Estimation of Ethyl Alcohol in Dilute Solutions (0·1 to 1%). Application of the Method to Urine. VILLEDIEU and HÉBERT (*J. Pharm. Chim.*, 1917, [vii], **15**, 41—44).—The iodometric method described depends on the fact that, at a definite dilution, the quantity of alcohol converted into iodoform is constant. Solutions are prepared containing quantities of alcohol varying from

0·1 to 1% of alcohol, and these solutions are treated as follows in order to obtain the value of the silver nitrate solution, used in the final titration, in terms of different quantities of alcohol. One hundred c.c. of the alcoholic solution are treated with 10 c.c. of 16% sodium hydroxide solution, and about 30 c.c. of 10·5% iodine solution are then added drop by drop. After three hours, a further small quantity of iodine solution is added, so that the mixture exhibits a yellow coloration, and, at the end of twenty-four hours, the precipitate is collected and washed with cold water. With the smaller quantities of alcohol it is necessary to seed the mixture with a trace of iodoform in order to promote precipitation. The filter and precipitate are now transferred to a flask, boiled for twenty minutes under a reflux apparatus with 30 c.c. of saturated alcoholic potassium hydroxide solution, the contents of the flask are then acidified with nitric acid, 20 c.c. of $N/100$-silver nitrate solution are added, and the excess of silver nitrate is titrated with $N/100$-thiocyanate solution. The number of c.c. of the silver nitrate solution required to precipitate the potassium iodide formed from the iodoform precipitates in the respective alcoholic solutions is thus obtained, and the numbers correspond with the quantities of alcohol present in the solutions. Any dilute alcoholic solution of unknown strength is treated similarly, and the alcohol content ascertained from the volume of silver nitrate required in the final titration. To estimate alcohol in urine, 200 c.c. of the sample, which must be free from acetone and aldehydes, are distilled after the addition of 1 c.c. of phosphoric acid, and 100 c.c. of distillate are collected and treated as described. W. P. S.

Analytical Differentiation between Fermented Sweet Wines and "Mistelles." W. I. BARAGIOLA and CH. GODET (*Zeitsch. anal. Chem.*, 1916, **55**, 561—577. Compare A., 1903, ii, 689).—Fifteen samples of "mistelles" (wines prepared by adding alcohol to grape juice) and eleven samples of fermented sweet wines were analysed, estimations being made of the quantities of ether-soluble acids, lactic acid, ammoniacal nitrogen, lævulose, dextrose, glycerol, ash, etc., present, but the results obtained show that the present analytical processes do not afford any means of distinguishing between these two classes of wines. W. P. S.

Estimation of Phloroglucinol and Resorcinol by means of Furfuraldehyde. EMIL VOTOČEK (*Ber.*, 1916, **49**, 2546—2547. Compare A., 1916, ii, 542).—An acknowledgment that the essentials of the author's process for the estimation of phloroglucinol were embodied in a paper by Welbel and Zeisel (A., 1895, ii, 426) which he had overlooked. J. C. W.

Colorimetric Methods for Estimating Cholesterol in Serum. PAUL G. WESTON (*J. Biol. Chem.*, 1917, **28**, 383—387). —The author describes a new colorimetric method for the estimation of cholesterol in serum in which the serum is boiled for two hours with 25% potassium hydroxide solution, and is then treated,

after concentration, with a saturated solution of calcium hydroxide. The resulting precipitate is collected, dried, and extracted with chloroform, and the extracted cholesterol then estimated by the colour produced on adding sulphuric acid to its solution in chloroform.

Six methods for the estimation of cholesterol are applied to a sample of serum, to a portion of which a known quantity of cholesterol is added. Uniformly consistent results are obtained by the methods of Autenrieth and Funk, Weston and Kent, Csonka, Gettler and Baker, and Weston, whilst Bloor's method yields very variable and inaccurate results. H. W. B.

Analysis of Honey and other Substances containing Lævulose. W. R. G. ATKINS (*Analyst*, 1917, **42**, 12—13).—The bromine oxidation method described by Wilson and Atkins (A., 1916, ii, 652) is recommended. An excess of bromine is added to the solution containing dextrose, lævulose, and maltose; sulphuric acid is then introduced in quantity sufficient to render the solution decinormal, and the mixture is shaken for forty-two hours. After this time, the excess of bromine is removed by the addition of sulphurous acid, the solution is nearly neutralised with potassium carbonate, and the reducing power of an aliquot portion is estimated by Kendall's method (A., 1912, ii, 393). Under these conditions of oxidation, a loss of about 1% of the lævulose takes place, but this loss is balanced by the small quantities of dextrose and maltose which remain unaffected. If only dextrose and lævulose are present, as in the case of honey, it is sufficient to estimate the reducing power before and after oxidation. Sucrose, when present, is estimated separately from the reducing power before and after inversion. Oxidation should be made on the inverted solution, allowance being made for the dextrose and lævulose formed from the sucrose. W. P. S.

Estimation of the Volatile Fatty Acids. Colorimetric Qualitative Reactions for their Identification. D. C. DYER (*J. Biol. Chem.*, 1917, **28**, 445—473).—The method described by the author is one of steam distillation, in which the aqueous solution containing the acid or acids is maintained throughout the course of the distillation at a constant volume of 150 c.c. In these circumstances, the "distilling constants," that is, the percentage amounts of the acid distilled in successive 10 c.c. or 100 c.c. of distillate, when plotted on a logarithmic chart, are indicated by a straight line when only one acid is present, and, in the case of two or more volatile acids, by a curved line which eventually becomes a straight line parallel to the line representing the lowest acid of the series present in the mixture.

For the identification of a single acid by this method, the total amount of acid present is first estimated by titration with standard alkali and the distillation then arranged so that the total 150 c.c. volume in the distilling flask contains about 0·5 c.c. of the pure acid. The acid is now liberated by the addition of an equivalent amount of sulphuric acid, and the distillation with steam com-

menced. When a convenient amount of distillate, say, 100 c.c., has collected, it is titrated with the standard alkali, and the percentage amount of acid which has distilled thus determined. This constitutes the distilling constant of the acid for the first 100 c.c. of distillate, and reference to the chart immediately reveals the nature of the acid present.

Examples are given showing the application of the method for the estimation of mixtures of two volatile fatty acids; and, in addition, a series of tests is described, depending on the difference in solubility of the iron and copper salts of the acids in various organic solvents, which serves to identify the acids in the distillate and to check the results of the distillation with steam. H. W. B.

Estimation of Free Sulphuric, Nitric, and Picric Acids in the Presence of each other. F. W. RICHARDSON (*J. Soc. Chem. Ind.*, 1917, **36**, 13—15).—The methods described are more particularly intended for the estimation of small quantities of the acids in effluents from picric acid works. The picric acid is estimated colorimetrically in a Lovibond tintometer, the yellow units of this instrument having been standardised previously against solutions containing definite quantities of picric acid. The observations must always be made at the same temperature, since the colour of picric acid solutions varies in depth with change of temperature. The nitric acid is also estimated colorimetrically by means of the phenoldisulphonic acid reaction, the colorations being observed in the tintometer; allowance is made for the colour contributed by the picric acid. The acidity of the three acids together is found by titrating a portion of the water with $N/10$-sodium hydroxide solution, using methyl-red as indicator; the acidity due to the picric and nitric acids is calculated and deducted, and the remaining acidity represents the quantity of sulphuric acid present.

It was found by experiment that waters containing sulphuric acid or nitric acid, or both, attacked iron, and when the water was used in boilers extensive corrosion occurred. Dilute picric acid solution also attacked iron readily. W. P. S.

Detection of Picric Acid and its Derivatives. HENRI PECKER (*J. Pharm. Chim.*, 1917, [vii], **15**, 70—74).—Urine containing picric acid or picramic acid gives a red coloration when rendered ammoniacal and brought into contact with ferrous sulphate–tartaric acid solution. The test gives the best results when made as a ring-test, and will detect the presence of 2 mg. of picric acid or picramic acid per litre of urine. By diluting a urine with definite quantities of water until the reaction is just observable, the quantity of the two acids present may be estimated approximately. The picric and picramic acids may be extracted previously with ether, after the urine has been oxidised; when the two acids are dyed on to wool, the picric acid is more readily extracted from the wool by ammonia than is picramic acid. The diazo-reaction described previously by the author (A., 1916, ii, 353) will detect as little as 0·05 mg. of picramic acid per litre of urine.

W. P. S.

Characterisation of Urotropine. P. CARLES (*Ann. Chim. anal.*, 1917, **22**, 8—9).—Urotropine (hexamethylenetetramine) is soluble in water, the solution being neutral to litmus; the substance should be free from chlorides and sulphates, and volatilise completely when heated. A red coloration is obtained when 0·1 gram of hexamethylenetetramine is heated with the addition of 0·1 gram of salicylic acid and 5 c.c. of sulphuric acid. If a 10% solution of hexamethylenetetramine is treated with one-fourth of its volume of sodium hypobromite solution and the mixture then neutralised with hydrochloric acid, a yellow precipitate is formed. W. P. S.

Estimation of Amino-nitrogen in Blood. JOSEPH C. BOCK (*J. Biol. Chem.*, 1917, **28**, 357—368).—The best precipitant for the removal of the proteins of the blood prior to the estimation of the amino-nitrogen is found to be trichloroacetic acid. Alcohol and phosphotungstic acid both give good precipitates, but they appear to retain traces of the amino-acids, so that the filtrates contain less amino-nitrogen than that which is obtained when trichloroacetic acid is employed. H. W. B.

Estimation of Dicyanodiamide in Nitrolime. A. STUTZER (*Zeitsch. angew. Chem.*, 1916, **29**, 417—418).—Since water is an unsuitable medium for extracting nitrolime (compare A., 1916, i, 548), the use of alcohol is recommended. Alcohol dissolves the free cyanamide and the dicyanodiamide completely, whilst only traces of nitrolime pass into solution. Ten grams of the nitrolime should be shaken for two hours with 100 c.c. of 94% alcohol, the mixture then filtered, and the total nitrogen estimated in 20 c.c. of the filtrate. Another portion of 50 c.c. of the filtrate is treated with 180 c.c. of water, 10 c.c. of 10% silver nitrate solution, and 10 c.c. of 10% ammonia; the free cyanamide is thus precipitated as its silver compound and the precipitate is collected on a filter. Two hundred c.c. of the filtrate from this precipitate are then treated with 50 c.c. of 10% sodium hydroxide solution, and, without heating, the precipitated silver dicyanodiamide is collected, washed, and the nitrogen in it is estimated in the usual way. The nitrogen in the silver cyanamide precipitate may also be estimated; this precipitate should not be washed until the filtrate has been collected for the estimation of the dicyanodiamide. The procedure given decreases the loss which takes place when silver dicyanodiamide is heated with sodium hydroxide to expel ammonia. W. P. S.

Impure Picric Acid as a Source of Error in the Estimation of Creatine and Creatinine. OTTO FOLIN and E. A. DOISY (*J. Biol. Chem.*, 1917, **28**, 349—356. Compare Hunter and Campbell, this vol., ii, 110).—The authors find that the observations on Folin's method of creatinine estimation published by McCrudden and Sargent (A., 1916, ii, 358, 587) were obtained by the use of an extraordinarily impure picric acid. When pure picric acid is employed, the irregularities obtained by McCrudden and Sargent do not occur. A method for the preparation of pure picric acid from

the commercial material is described, which depends on the repeated salting out of sodium picrate by the addition of sodium chloride to the hot alkaline solution. The picric acid is subsequently liberated from the purified picrate by sulphuric acid.

While the findings of McCrudden and Sargent are abundantly accounted for on the basis of impurities in their picric acid, the fact remains that the yellow colour of pure sodium picrate does limit the dilution in which creatinine may be estimated by the colorimetric method. A modification of the method is therefore described for dilute creatinine solutions in which the excess of picric acid is removed by the addition of a solution containing 7% potassium hydroxide and 25% potassium chloride. Most of the picric acid is precipitated as the potassium salt, and therefore after centrifugalisation the colour due to the creatinine in the clear liquid is made more predominant. The standard creatinine solution must be similarly treated before the comparison is made.

The presence of a second substance of creatinine nature in urine, reported by McCrudden and Sargent (*loc. cit.*), is disproved, and admitted by McCrudden and Sargent to be incorrect. H. W. B.

Sensitive Reaction of the Alkaloids of the Solanaceæ. ANON. (*J. Pharm. Chim.*, 1917, [vii], **15**, 54; from *Pharmazevtizeski J.*, 1916, 263).—An intense reddish-violet coloration is obtained when a trace of an alkaloid from the *Solanaceae* is heated with a drop of a mixture consisting of *p*-dimethylaminobenzaldehyde, 2 grams, concentrated sulphuric acid, 6 grams, and water, 0·4 gram; the reaction may be obtained with 0·0002 mg. of the alkaloids. Atropine, hyoscyamine, and scopolamine behave identically with the reagent. Codeine and morphine yield a red coloration in the cold; quinine, a reddish-brown coloration; eserine and veratrine, green colorations; and narcotine and papaverine, orange colorations. W. P. S.

Preparation of Hide Powder. Y. S. ZALKIND and N. I. EGORKIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 302—304).—The authors describe a method for preparing hide powder suitable for determining the content of tannins in tanning extracts, such powder being difficult to purchase under existing conditions. T. H. P.

General and Physical Chemistry.

New Lines in the Spectrum of Magnesium. MIGUEL CATALÁN SAÑUDO (*Anal. Fis. Quim.*, 1916, **14**, 584—596).—The presence of twelve new lines in the arc spectrum of magnesium in air has been proved, as well as the existence of two different spectra for the metal and its oxide. A. J. W.

Dispersion and the Size of Molecules of Hydrogen, Oxygen, and Nitrogen. L. SILBERSTEIN (*Phil. Mag.*, 1917, [vi], **33**, 215—222).—By application of the theory of dispersion the author has calculated the distance between the atoms in the molecules of hydrogen, oxygen, and nitrogen. This method gives $1\cdot067 \times 10^{-8}$ cm. for hydrogen, $1\cdot265 \times 10^{-8}$ cm. for oxygen, and $1\cdot493 \times 10^{-8}$ cm. for nitrogen. Incidentally, it is found that the number of dispersive electrons in the atoms of hydrogen, oxygen, and nitrogen is the same as the normal valency. The above values of the inter-atomic distances are in agreement with the radii of the respective molecules as found by methods based on the kinetic theory. H. M. D.

Absorption-coefficient of Solutions of Cobalt Chloride in Water and various Alcohols for Monochromatic Radiation. E. O. HULBERT, J. F. HUTCHINSON, and H. C. JONES (*J. Physical Chem.*, 1917, **21**, 150—164).—The authors have carried out a large number of experiments on the absorption of monochromatic light by solutions of cobalt chloride in water, methyl alcohol, ethyl alcohol, propyl alcohol, *iso*butyl alcohol, and *iso*amyl alcohol. The measurements were made at intervals of 20—40 $\mu\mu$ over the range 600 $\mu\mu$—1300 $\mu\mu$, and with solutions of varying concentration at the ordinary temperature. The value of A, the molecular absorption-coefficient, has been calculated from all measurements by the formula $A = (\alpha - \alpha_0)/c$, where α is the absorption-coefficient of the solution, α_0 that of the solvent, and c the molecular concentration. It is shown that in the region of wave-lengths lying on the long wave-length edge of the yellowish-red absorption band the A—c curves show that A decreases with dilution. In the case of aqueous solutions this decrease is considerable, and in the alcoholic solutions the decrease becomes more and more marked the greater the molecular complexity of the alcohol. This is in complete accord with the previously published work of Jones and Anderson (Carnegie Inst. of Washington Publications, No. 110). In the region of low absorption between the two bands A is constant, but in many cases the value of α is so small that deductions as to the value of A are not very trustworthy. In the region of wave-lengths lying on the edge of the infra-red band, A shows variations, and these variations show a regularity which is concomitant with the molecular com-

plexity of the solvent. In this region A is nearly constant for the aqueous solutions, but increases with dilution for the alcohol solutions, the increase becoming greater as the molecular weight of the alcohol increases. In certain cases A decreases to a minimum with dilution and then increases again, but in no case was A found to increase to a maximum and then decrease. At present no theory is advanced to explain these facts, but the fact that A varies with c has probably been correctly attributed by Jones and Anderson (*loc. cit.*) and others to the formation of complexes, which were considered to be loose chemical compounds of molecules of the salt with molecules of the solvent. It is unquestionable that the changes recorded in the present paper may be explained in a qualitative manner by the solvate hypothesis. J. F. S.

Positive Ionisation of certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures. A. T. WATERMAN (*Phil. Mag.*, 1917, [vi], **33**, 225—247).—Making use of the method employed by Richardson (A., 1913, ii, 910), the author has examined the positive emission of the following hot salts: silver chloride, silver bromide, lead chloride, lead bromide, cuprous chloride, cupric chloride, aluminium fluoride, platinous chloride, and molybdenite, with the object of ascertaining whether any relationship exists between the valency of the metal and the charges on the ions composing the positive emission. It is shown that silver chloride, silver bromide, lead chloride, lead bromide, platinous chloride, and cupric chloride do not give rise to characteristic positive emissions. The same is probably true for aluminium fluoride. In the case of cuprous chloride there are indications that the ion Cu^{++} is expelled. In nearly every case examined positive ions have been found to be present, for which the value of e/m corresponds with singly charged atoms, either of potassium or of sodium or of both these elements; the results therefore confirm those of Richardson (*loc. cit.*). It is possible that the characteristic emission from these salts does occur, but is too small for measurement with the apparatus used. Molybdenite has been found to possess the following interesting electrical properties. 1. In the range of temperature between the ordinary and a brilliant red heat this mineral exists in two distinct states. 2. The resistance in the low voltage or low temperature state is very nearly an inverse exponential function of the absolute temperature. 3. At the ordinary temperature the resistance is a function of the applied potential difference, and appears to approach an infinite value as the potential approaches zero. 4. The conduction of electricity is evidently carried on by electrons. 5. With regard to the thermo-ionic emission from molybdenite it is noted that a large emission (mainly K^+ emission) takes place from impurities, and that a characteristic emission of Mo^+ ions also occurs, which apparently has no exclusive relationship to the break or to either state. J. F. S.

Chemical Composition versus Electrical Conductivity. COLIN G. FINK (*J. Physical Chem.*, 1917, **21**, 32—36).—The electrical conductivity of mixtures of finely divided substances is a function of the relative size of the constituent particles. Observations made with mixtures of equal weights of finely powdered tungsten and thoria, which were made into rods and fired at 1600° for three hours, show very large differences in the conductivity.

H. M. D.

Some Particular Cases of Current-potential Lines. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 653—670).—A theoretical paper, in which the author considers the form of the curve connecting the electrode potential with the current density. Assuming that the ion concentration in the solution outside the diffusion layer is C and the concentration at the electrode is c, the thickness of the diffusion layer being δ, then the quantity of ions passing per second through 1 cm.^{2} of cross-section is given by $D/86400 \, . \, (C-c)/\delta$, in which D is the coefficient of diffusion. The charge carried by these ions is equal to the current density d, which is therefore given by $d = 1{\cdot}117D(C-c)/\delta$. By substitution in the equation for the electrode potential, this may be written in the form $E = \epsilon + 0{\cdot}058/n \, . \, \log(C - d\delta/1{\cdot}117D)$.

For the limiting value $c=0$, the current density has a maximum value given by $d_{max.} = 1{\cdot}117DC/\delta$, according to which the limiting current is proportional to the ion concentration of the solution and to the diffusion-coefficient and inversely proportional to the thickness of the diffusion layer.

The theoretical equations are applied in the discussion of experimental results and in the consideration of the influence of the presence of complex or hydrated ions. The case of the discharge of halogen ions at a silver anode is examined in detail. H. M. D.

An Apparatus for Determining Freezing Point Lowering. R. G. VAN NAME and W. G. BROWN (*Amer. J. Sci.*, 1917, [iv], **43**, 110—114).—The containing vessel consists of a vacuum-walled tube of about 500 c.c. capacity, surrounded by a projecting jacket of tin and closed by a cork perforated to admit the Beckmann thermometer, the stem of the glass stirrer, a short tube through which the liquid may be inoculated, and a cooling tube.

The cooling tube represents the chief novelty in the apparatus. It consists of two concentric glass tubes through which cold brine is circulated, the cooling liquid passing down the inner tube and up between the inner and outer tubes, whence it emerges through a side-tube. When the desired degree of undercooling has been obtained, the inner tube is lowered so as to close the end of this tube, and this movement uncovers a hole in the upper part of the inner tube, with the result that the brine only circulates through the upper portion of the cooling tube which projects from the apparatus. To prevent the deposition of hoar frost on the part of the cooling tube above the level of the liquid, the upper portion of this tube, down to a point below the surface of the liquid, is

surrounded by a narrow vacuum jacket. This arrangement permits the employment of a much colder brine for cooling purposes and increases the rapidity of the freezing-point determination.

Data are recorded for solutions of sucrose, which show that the apparatus yields concordant and satisfactory results. H. M. D.

The Relation of Oxygen to the Heat of Combustion of Organic Compounds. W. M. THORNTON (*Phil. Mag.*, 1917, [vi], **33**, 196—203).—If H is the heat of combustion and n the number of oxygen atoms required for the complete combustion of an organic compound, the value of H/n is found to be more or less independent of the nature of the compound. The mean value of H/n according to the data for paraffin, unsaturated and aromatic hydrocarbons, halogen compounds, ethers and acetals, alcohols, aldehydes and ketones, acids, esters, mercaptans, sulphides, thiocyanates, cyanogen, hydrogen cyanide, nitriles, and amines is equal to 53.

The nitro-compounds are anomalous in that H/n has a higher value, but if n is taken to represent the oxygen which is required to burn the carbon and hydrogen, the value of H/n is in agreement with the above mean. This would seem to show that the oxygen in these nitro-compounds takes no part in the combustion process, and this may be due to the difficulty of activating the oxygen when associated with nitrogen so that the combustion is effected by free oxygen.

From the relation $H=53n$, it is possible to calculate the quantity of air required for the combustion of any hydrocarbon mixture of unknown composition if the heat of combustion and the vapour density are known. Conversely, if the calorific value of any liquid or gaseous fuel is required, it may be calculated from the volume of air which is required to burn completely a measured volume of the vapour of known density. H. M. D.

Heat of Dilution of Alcohol in Benzene. WILLIS A. GIBBONS (*J. Physical Chem.*, 1917, **21**, 48—74).—In applying the formulæ for the changes in the vapour pressure, freezing point, and boiling point produced by a solute to calculate the molecular weight of the latter, it is customary to ignore the influence of the heat of dilution. According to Beckmann's determinations (A., 1889, 11) of the molecular weight of ethyl alcohol in benzene solution by the freezing-point method, the molecular weight increases from the normal value in dilute solution to a value about seven times as large in concentrated solution. The heat of dilution in this case is very large, and with the object of determining the connexion between the heat of dilution and abnormal changes in the vapour pressure, the author has made a detailed investigation of the variation of the heat of dilution with the concentration by experiments with solutions of alcohol in benzene.

The apparatus used was an isothermal calorimeter the use of which minimises the errors which are peculiar to the ordinary calorimeter and avoids also a correction for water equivalent.

Observations were made at 10°, 20°, and 30°, and it is found that the results may be expressed by a formula of the type $x=-(bQ^2+cQ)/(Q-a)$, in which a, b, and c are constants, Q is the molecular heat of dilution, and x is the number of mols. of solvent (benzene) per mol. of solute (alcohol). The minus sign denotes the fact that heat is absorbed in the dilution of the solutions.

In the final part of the paper an attempt is made to apply the results as a correction to the ordinary molecular weight formula, but the results obtained lead to the conclusion that the theoretical relations are not sufficiently developed to permit of this being done in a proper manner. It seems, however, that the molecular weight will always be too large when heat is absorbed on dilution and too small when dilution is accompanied by development of heat.

H. M. D.

Relationship between the Physical Properties of Isomeric Cobaltammines and the Electro-valencies of their Co-ordination Complexes. Rajendra Lal De (T., 1917, **111**, 51—54).—In order to ascertain the influence of electro-valency on the volume occupied by a substance, the author has determined the densities of the isomerides: triamminecobalt nitrate, dinitrotetra-amminecobalti–tetranitrodiamminecobaltiate, and hexa-ammine-cobalti–hexanitrocobaltiate, the electro-valencies of which are respectively zero, one, and three. The molecular volume at 32—33° increases with the electro-valency, the two increments being nearly equal. The two stereoisomeric forms 1 : 2 and 1 : 6 of the second isomeride have the same molecular volume.

The solubilities of the isomerides in water at the ordinary temperature were also determined. Of the two stereoisomeric forms of the second compound, the 1 : 2 compound is 9·3 times as soluble as the 1 : 6 form. The influence of spacial configuration on the solubility seems to be of more importance than the electro-valency.

H. M. D.

Molecular Attraction. XIII. J. E. Mills (*J. Physical Chem.*, 1917, **21**, 101—106).—Polemical against Matthews (A., 1916, ii, 600); it is shown that Matthews in his discussion of the Dietrici, Mills, and van der Waals's equations simply substitutes for the internal pressure term (a/v^2) in the van der Waals equation, the more correct expressions derived by the author. Consequently, his conclusions with regard to these equations are incorrect. A number of other errors are pointed out. It is also shown that these errors do not in any way invalidate the discussion or the results arrived at from the relationships of Goldhammer and Eötvos on the attractive forces of the molecules.

J. F. S.

The Detergent Action of Soap. Spencer Umfreville Pickering (T., 1917, **111**, 86—101).—Although the detergent action of soap is partly due to its power of emulsifying oil and partly to the low value of the surface tension between oil and soap solution, it seems probable that the detergent effect is influenced to a greater extent by the solubility of oil in soap solutions.

The behaviour of paraffin oil and benzene towards various soaps in admixture with varying quantities of water has been examined, and these observations lead to the conclusion that soluble compounds of oil and soap are formed which are not decomposed by the addition of further water. If the soap is diluted previous to its treatment with oil, the extent to which combination occurs is much smaller, the reduction being attributable to the increase in the emulsification of the oil. The nature of the resulting system varies from a limpid liquid compound to an almost solid emulsion. The proportions in which oil and soap combine together depend on the chemical as well as the physical nature of the reagents.

Experiments made with naphthalene and soap show that this hydrocarbon behaves quite differently from paraffin oil. It dissolves to a small extent in heated soap, but some of this crystallises out on cooling. The solubility is increased by the addition of a little water, but diminishes on further dilution. In presence of naphthalene, the quantity of paraffin oil dissolved by soap diminishes. H. M. D.

Crystallography and Röntgen Rays. M. VON LAUE (*Ber.*, 1917, **50**, 8—20).—A lecture delivered before the German Chemical Society on November 11th, 1916, dealing with the space-lattice structure of crystals. J. C. W.

The Ultimate Structure of Crystals. F. RINNE, (*Jahrb. Min.*, 1916, ii, 47—108).—A theoretical paper in which the author discusses the recent application of *X*-rays to the study of crystals. Alongside the science of stereochemistry is developing a stereophysics, and these, together with the study of crystal structure, form a new branch of science, which the author terms "Feinbaulehre der Materie" (the study of the ultimate structure of matter), or Leptonology (λεπτός). Whether the crystal be considered as an atomic structure, or as containing groups of atoms or molecules, the influence of electrons on the structure must soon be brought under consideration. Debye has already studied the constitution of the hydrogen molecule (*Ber. Akad. München*, 1915) and of the liquid benzene molecule (Debye and Scherrer, *Nachr. Ges. Wiss. Göttingen Math.-phys. Kl.*, 1916) by means of *X*-rays. The diameter of the benzene molecule he finds to be $12\cdot4 \times 10^{-8}$ cm. and its thickness at most $1\cdot9 \times 10^{-8}$ cm. The different forms of matter, gas, liquid, liquid crystal, and crystal form a continuous series, and each in turn is discussed by the author. In liquid crystals, the particles are orientated regularly with respect to one axis. It is suggested that the molecules become orientated with their principal axes parallel, giving a close approximation to an optically uniaxial crystal (compare this vol., ii, 18). The growth of a crystal is attributed to the special properties of the surface layer. The atoms in the superficial zone of imperfectly crystalline material have some of their valencies unsaturated, whereby fresh material can be attracted.

A considerable number of Laue diagrams are included in the

paper, illustrative of olivine, sucrose, cordierite, oligoclase, muscovite, aragonite, calcspar, albite, and anorthite, and are employed in a discussion of the phenomena of isomorphism, polymorphism, and morphotropy. E. H. R.

The Reversibility of Sulphide Sols and the Protective Action of Hydrogen Sulphide. S. W. YOUNG and WIN R. GODDARD (*J. Physical Chem.*, 1917, **21**, 1—13).—A dialysing apparatus is described which has been employed in the investigation of the influence of hydrogen sulphide on the stability of colloidal solutions of metallic sulphides. The results obtained with cadmium, zinc, lead, arsenic, and mercuric sulphides show that the removal of hydrogen sulphide by dialysis causes coagulation of the metallic sulphide, but that the coagulated sol is redispersed when hydrogen is again introduced into the solution. It would seem that the coagulation and dispersion are determined by the concentration of the hydrogen sulphide.

In experiments made with zinc sulphide, it was found that the dispersive power of the hydrogen sulphide increases up to a pressure of 1·5—2 atmospheres, and then decreases somewhat as the pressure is further increased. The dispersive power of hydrogen sulphide is also shown by the results of experiments in which potassium chloride in varying quantities was added to the colloidal zinc sulphide. The coagulate obtained by raising the temperature of the sol is also dispersed under the influence of hydrogen sulphide. H. M. D.

Colloidal Solutions of Copper Sulphide. S. W. YOUNG and ROLAND NEAL (*J. Physical Chem.*, 1917, **21**, 14—31).—The properties of copper sulphide sols have been examined, the experiments being designed to show the influence of electrolytes and of hydrogen sulphide on the coagulation of the sols and on the mobility of the colloidal particles.

Colloidal solutions were prepared by the agitation of well-washed copper hydroxide, copper carbonate, or freshly precipitated copper sulphide with aqueous hydrogen sulphide. The coagulation experiments show that the concentration of a given electrolyte, which is required to produce coagulation within twenty-four hours, is independent of the mode of preparation of the sol, of the presence or absence of free hydrogen sulphide, and within wide limits is independent of the concentration of the colloidal solution. The relative coagulating powers of the chlorides of potassium, calcium, and aluminium are as 1 : 39 : 875. Sols which have been freed from hydrogen sulphide are unstable, and when kept for some months undergo spontaneous coagulation, but so far as the influence of electrolytes is concerned, the behaviour of the sols is the same whether hydrogen sulphide is present or not.

The mobility of the colloidal particles in an electric field varies according to the mode of preparation. The mobility is increased in the presence of electrolytes, but the increase bears no apparent relation to the coagulating power of the electrolyte used. On the other hand, the increase in the mobility seems to depend on the

mobility of the particles in the original sol. The mobility of the particles of a particular sol increases with the dilution, and is greatly reduced by hydrogen sulphide. Removal of the hydrogen sulphide restores the sol to its original condition, and the change is therefore reversible. The effect produced by bubbling air or oxygen through the sol can be entirely explained by the removal of hydrogen sulphide.

It is suggested that the formation of colloidal solutions of copper sulphide may play a part in the processes which are involved in the secondary enrichment of gels of copper sulphide ore.

H. M. D.

The Action of Mercuric Chloride on Gold Hydrosols. O. HERSTAD (*Koll. Chem. Beihefte*, 1916, **8**, 399—424).—According to previous observations, the coagulating power of mercuric chloride towards gold sols is greater than that of most salts of the heavy metals. The action does not occur if hydrochloric acid is added to the mercuric chloride solution. In view of the fact that mercuric chloride is only slightly ionised, its behaviour is rather remarkable, and a further examination of the phenomena has been undertaken with colloidal gold solutions prepared by the action of formaldehyde.

These experiments show that coagulation of gold sols by mercuric chloride is inhibited by the addition of acid, and the effect is also not observed if the sol is dialysed or boiled before the mercuric chloride is added. By means of electrometric measurements, it has been found that coagulation only occurs in the case of sols which are slightly alkaline. The hydrion concentration, which is sufficient to prevent coagulation, varies with the concentration of the mercuric chloride. For a given hydrion concentration, there is an upper as well as a lower limiting value of the mercuric chloride concentration which produces coagulation, and if a diagram is constructed by plotting hydrochloric acid concentration on the abscissa and mercuric chloride concentration on the ordinate, the coagulating mixtures fall within a zone which is bounded by the ordinate and by two intersecting curves which represent the upper and lower limiting values of the mercuric chloride concentration.

It is supposed that the coagulating power of mercuric chloride is due to mercuric oxide (or mercurous oxide), which forms an envelope round the colloidal gold particles and transforms the negative colloid into a positive colloid.

The gold sols afford evidence of ageing in that they gradually become less sensitive to mercuric chloride, and this is supposed to be the result of a slow oxidation of the gold by the formaldehyde present.

H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. II. Colloidal Silver. A. GUTBIER and A. WAGNER (*Kolloid Zeitsch.*, 1916, **19**, 280—287. Compare this vol., ii, 131).—The action of quince seed extract as a protective colloid has been examined in experiments with silver sols prepared by the reduction of silver nitrate by hydrazine hydrate in presence of the organic

colloid. By dialysing the resulting colloidal silver solution and evaporating at low temperature or precipitating by the addition of alcohol, solid substances have been obtained containing about 20% of silver, which dissolve completely in water.

Reversible colloids of the same kind were also obtained by the action of sunlight on silver nitrate solutions in presence of the quince seed extract. The coagulation of these protected silver sols by the action of various electrolytes has been examined, and the results indicate that the coagulating power diminishes in the order: sulphuric acid, sodium chloride, sodium carbonate, sodium hydroxide. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. III. Colloidal Gold. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 287—291).—Experiments similar to those recorded in the previous paper have shown that solid substances which contain up to 50% of gold and are completely soluble in water may be obtained by the reduction of gold chloride by hydrazine hydrate in presence of quince seed extract. The protective action of the organic colloid on the gold sols is very pronounced. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. IV. Colloidal Mercury. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 291—297).—The protective action of quince seed extract on colloidal solutions of mercury prepared by the action of hydrazine hydrate on mercuric chloride is not very marked. If, however, sodium hyposulphite is used as the reducing agent, much more stable solutions are obtained, and by dialysing and evaporating or precipitating with alcohol, solid colloids containing up to about 20% of metallic mercury have been prepared which are partly soluble in water. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. V. Colloidal Platinum. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 298—302).—Platinum sols, prepared by the reducing action of hydrazine hydrate on platinum chloride in presence of quince seed extract, yield, on dialysing and evaporating or precipitating by the addition of alcohol, solid colloidal substances which contain as much as 25% of platinum. These colloids are readily soluble in warm water. As in the case of silver, gold, and mercury, the protective action of quince seed extract on colloidal platinum is strongly marked. The coagulation phenomena associated with the presence of electrolytes has also been examined. H. M. D.

Non-, Uni- and Bi-variant Equilibria. XI. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 713—727. Compare this vol., ii, 132).—A further theoretical consideration of the equilibrium relations in binary systems with two indifferent phases. For any binary system in which two indifferent

phases occur there are two types of pressure–temperature diagram, and the author shows how these may be derived. H. M. D.

The Influence of Temperature on Chemical Equilibria. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 636—649).—The integration of the equation $d \log K/dT = Q/RT^2$ leads to various formulæ expressing the connexion between the equilibrium constant of a reversible chemical change and the temperature, the nature of which depends on the assumed relation between the heat of reaction, Q, and the temperature, T. If the algebraic sum of the heat capacities of the systems on the two sides of the equation is zero at all temperatures, the integrated equation is of the form $\log K = a/T + b$, in which a and b are constants.

The author maintains that this equation is in satisfactory agreement with the experimental data for many gas reactions. Although for such systems the algebraic sum of the heat capacities of the reacting substances is not in general equal to zero, yet the influence of this factor is in most cases so small that the error which is involved in the assumption of the zero value is not nearly so large as the errors incidental to the equilibrium measurements. On this account it is claimed that the above equation is to be preferred to the more complicated expressions which are frequently used to represent the variation of the position of chemical equilibrium with the temperature.

The validity of the argument is supported by a comparison of the values of $\log K$ afforded by the experimental data for the reactions $2CO_2 \rightleftarrows 2CO + O_2$ and $2HI \rightleftarrows H_2 + I_2$ with those which have been calculated from the simple equation and from more complicated expressions.

Reactions in which solid substances take part may be expected to show greater deviations from the requirements of the simple formula. In this connexion the author has examined the data corresponding with the equilibria $Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2$, $FeO + CO \rightleftarrows Fe + CO_2$, and $Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2$, and comes to the conclusion that the available data are untrustworthy. According to Bauer and Glässner (A., 1903, ii, 423), the curve for the equilibrium $FeO + CO \rightleftarrows Fe + CO_2$ shows a minimum at 680°. At this temperature the heat of reaction is zero, whereas at 585° it is -3114 cal. and $+8724$ cal. at 835°. The heat of reaction, according to this, changes to the extent of 11,838 cal. for a change of temperature of 250°. This would correspond with a value of 47·3 cal. for the algebraic sum of the heat capacities of the reacting substances, a value which is much too large to be accepted as possible. Similar relations are found when the data for the other equilibria are examined, and for this reason the author considers that the recorded numbers are not nearly so accurate as has been assumed.

A further case of equilibrium examined is the dissociation of ammonium bromide, the constant for which, according to Smith and Lombard (A., 1915, ii, 86), shows a maximum at about 320°.

At higher temperatures heat is apparently developed in the dissociation process, and at 384° the calculated heat of reaction is 43,000 cal. This change in the heat of reaction for a temperature variation of 64° corresponds with a value of 670 cal. for the algebraic sum of the heat capacities of the ammonium bromide and its dissociation products. This value is much too large, and suggests that the experimental observations are inaccurate.

In the present state of our knowledge of gas equilibria it would therefore seem that the influence of temperature may be adequately represented by means of the formula which neglects the differences in the heat capacities of the reacting systems. H. M. D.

Influence of the Solvent on the Situation of the Homogeneous Equilibrium. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 708—712).—There is a great deal of evidence to show that the equilibrium which is set up between the substances involved in a reversible reaction varies with the nature of the solvent. This variation has not yet been satisfactorily explained, but the author shows by theoretical reasoning that the shift in the position of equilibrium in passing from one solvent to another must be ascribed to a difference in the heat of the reaction in the two solvents. This in its turn may be referred to differences in the heats of dissolution of the reacting substances in the solvents in question. If the reversible reaction is represented by $A \rightleftharpoons B$ and Q_A and Q_A' are the heats of dissolution of A in two different solvents, the corresponding heats of dissolution of B being Q_B and Q_B', then the relation between the equilibrium constants K and K' is given by $\log K/K' = \{(Q_A - Q_A') - (Q_B - Q_B')\}/RT$. H. M. D.

"Stepped" Ignition. RICHARD VERNON WHEELER (T., 1917, **111**, 130—138).—The ignition of inflammable mixtures of gases by the impulsive electrical discharge is stated by Thornton (A., 1914, ii, 524, 834) to be characterised by discontinuities which are observed when the composition of the mixture is varied at constant pressure or when a given gas mixture is examined under varying pressure.

Using a method of experiment of the same kind, the author has been unable to detect any discontinuity in the ignition of a 9·5% mixture of methane and air when the pressure was varied from 100 to 800 mm. The curves obtained by plotting the "igniting-currents" against the pressure are quite continuous. It would seem that the results obtained by Thornton require some condition of experiment which the author has been unable to reproduce or has been careful to exclude.

[With ALLAN GREENWELL.]—A mathematical analysis of the hyperbolic curve suggests that the quantities actually recorded are not really independent. The independent variables, as distinguished from the recorded variables, may be represented by employing inclined axes parallel to the asymptotes of the hyperbola, the origin remaining the same. The distance between the new ordinate and the relative asymptote represents the minimum ignition

pressure for any value of the current and the distance between the new abscissa and the relative asymptote gives the minimum igniting current for any degree of compression. The product of the real pressure minus the minimum pressure and the real igniting current minus the minimum igniting current is constant.

H. M. D.

Limits of Inflammability of Gaseous Mixtures. W. M. THORNTON (*Phil. Mag.*, 1917, [vi], **33**, 190—196).—According to previous experiments (compare A., 1914, ii, 834), the curve expressing the relation between the energy of the igniting current in impulsive spark or condenser discharge and the composition of a mixture of inflammable gas and air shows marked discontinuities for certain mixtures which are characterised by the fact that the ratio of the oxygen atoms to the molecules of inflammable gas is represented by a whole number. It is now shown that simple relations of the same kind are exhibited by the mixtures which correspond with the upper and lower limits of inflammability.

In the upper limit mixtures of the paraffin hydrocarbons there is twice as much inflammable gas as in that which corresponds with perfect combustion. In the case of acetylene, cyanogen, and carbon disulphide this ratio is equal to three, whilst for hydrogen it is five, and for carbon monoxide it is equal to six.

In respect of the lower limit of inflammability it is found that in the case of the hydrocarbons, ignition fails when the mixture contains twice as much oxygen as is required for complete combustion. If n is the number of oxygen atoms required for the combustion of one molecule of inflammable gas, the lower limiting mixture contains $2n-1$ atoms of oxygen. The ratio of the oxygen atoms in the lower limiting mixture to the normal number of oxygen atoms is, on the other hand, $(3n-2)/n$ for methyl alcohol, ethyl alcohol, acetylene, cyanogen, and carbon disulphide, $(n+1)/n$ for ethylene, 3 for hydrogen sulphide and carbon monoxide, and 9 for hydrogen.

If U is the percentage of inflammable gas in the upper limiting mixture, then $U \times n$ is approximately constant. Similarly, if L is the percentage of inflammable gas in the lower limiting mixture and n_L is the number of oxygen atoms per molecule of inflammable gas in this mixture, it is found that $L \times n_L$ is very nearly constant.

Since n is approximately proportional to the heat of combustion of the inflammable gas, it follows that the heat of combustion of unit volume is the same for all upper limit mixtures of inflammable gases. From the constancy of $L \times n_L$ it is also apparent that the number of oxygen atoms in unit volume of the lower limiting mixtures is the same for all inflammable gases.

Since $U \times n$ and $L \times n_L$ are constant, and n/n_L is approximately constant for homologous series of gases, it follows that the ratio of U/L should be nearly constant. The data for the paraffins show that this ratio increases slightly as the series is ascended, and remains constant in the ethylene series.

According to the above data, inflammation is determined by the

existence of certain numerical relations between the number of molecules of oxygen and of the inflammable gas, and it would seem that the upper and lower limits of inflammability are controlled by the heat liberated in the reaction. H. M. D.

Valency Centres. O. HINSBERG (*J. pr. Chem.*, 1916, [ii], **94**, 179—192).—A theoretical paper, in which the conception of different centres from which the forces of valency emanate is extended from the case of sulphur (A., 1916, i, 725) to account for many peculiarities of the oxygen, selenium, tellurium, nitrogen, or halogen atom. In general terms it is pointed out that elements with only one valency centre in the atom (for example, carbon) give neutral hydrides, but the acid nature of the hydrides and the basic nature of the onium compounds increase with the number of valency centres. Thus, sulphur and nitrogen, with two centres, give feebly acidic hydrides (H_2S and NH_3) and strongly basic onium compounds; iodine, with three centres, gives a strongly acid hydride and very strongly basic diaryliodonium hydroxides.

J. C. W.

New Laboratory Apparatus for the Evolution of Gas. B. ANGELI (*Boll. chim. farm.*, 1917, **56**, 2—3).—A modified Kipp apparatus is described, which functions with a small quantity of the reacting liquid, uses liquid always of the same purity, is easily dismounted, and has other advantages. Two forms are figured.

T. H. P.

Inorganic Chemistry.

The Allotropy of Phosphorus. J. W. Terwen (*Chem. Weekblad*, 1917, **14**, 180—197).—A review of the progress made in the chemistry of phosphorus during the last fifteen years, with a summary of the literature. A. J. W.

Combinations of Arsenious Oxide and Salts. I. and II. F. A. H. Schreinemakers and (Mej.) W. C. de Baat (*Chem. Weekblad*, 1917, **14**, 141—146, 203—208).—An application of Schreinemakers's graphic method to systems containing water and arsenious oxide with the bromides of lithium, sodium, potassium, and ammonium, and lithium chloride, potassium iodide, and the chlorides and bromides of calcium, barium, and strontium. A. J. W.

Density of Silicon Tetrafluoride. Albert F. O. Germann and Harold S. Booth (*J. Physical Chem.*, 1917, **21**, 81—100).—The authors have determined the density of silicon tetrafluoride which has been subjected to very careful purification. The gas

was prepared in a perfectly dry, evacuated apparatus in the usual way from calcium fluoride, silica, and sulphuric acid, and was led over glass wool to remove free hydrogen fluoride and over a column of phosphoric oxide. The gas thus dried was led into a receiver cooled by liquid air and solidified. The product was then melted and fractionally distilled at normal pressure and atmospheric temperature, and after several distillations led into weighed globes and weighed. The author points out that fractional sublimation under reduced pressure, as employed by Jaquerod and Tourpaian (A., 1913, ii, 401, 772), gives a product which is heavier than the product obtained in the present work by two parts per thousand. This is attributed to the presence of the sesquifluoride, Si_4F_6, due no doubt to the fact that Jaquerod and Tourpaian heated the reaction mixture in the preparation of the fluoride, whereas the present authors generated the gas without heat. The weighings were corrected for: (1) the contraction of the evacuated globes; (2) the buoyancy of the air on the weights and globes; (3) for the altitude and latitude; and (4) for the compressibility of the tetrafluoride. As the mean of eleven experiments, it is found that the weight of the normal litre of silicon tetrafluoride is $L_N = 4{\cdot}68397$ grams, which, since the fifth decimal is somewhat doubtful, may be taken as $L_N = 4{\cdot}6840$. J. F. S.

The System-Mercury Iodide. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 703—708).—Red mercuric iodide is transformed into the yellow modification at 127°. When this is heated further, it remains yellow up to about 190°, and then assumes a red tint, which deepens until the substance melts to a dark red liquid at 255·5°. Observations made with large crystals of yellow mercuric iodide show that the gradual development of the orange colour with rise of temperature is not accompanied by any change in the crystalline form. This fact points to the formation of mixed rhombic crystals containing both the yellow and red modifications, the proportion of the latter increasing with rise of temperature. It is suggested that there are two isomeric forms of mercuric iodide (α and β), and that the red and yellow modifications are mixed crystals containing the two forms in different proportions. The equilibrium relationships are examined from this point of view and represented on a temperature-concentration diagram. H. M. D.

The Luminescence of the Iodide of Millon's Base. HARRY B. WEISER (*J. Physical Chem.*, 1917, **21**, 37—47).—When the substance obtained by the action of ammonia on an alkaline solution of mercuric potassium iodide is heated, it decomposes, with the emission of violet light. The products formed are ammonia, mercuric iodide, nitrogen, water, and mercury. Ammonia is evolved at 160°, but the decomposition is not rapid below about 400°. The chemi-luminescence is associated with the rapid decomposition, the reaction being endothermic.

There are apparently three distinct luminescent effects in which

mercury or its compounds are involved. It is suggested that the orange luminescence is attributable to the change of the mercurous ion into non-ionised mercurous salt, the green luminescence to the change of mercurous ion into mercuric ion, and the violet luminescence to the conversion of mercuric ion into the mercury atom.

H. M. D.

The Action of Potassium Permanganate on the Metals. WILLIAM FOSTER (*Chem. News*, 1917, **115**, 73).—The reduction of potassium permanganate solution by hydrogen in presence of platinum black is sometimes shown as a lecture experiment. Neutral dilute solutions are reduced by many metals, including gold and platinum, even without hydrogen. The solution becomes alkaline, showing the formation of potassium hydroxide, and in some cases the formation of manganate may be observed. Silver reduces quickly, whilst tungsten acts rapidly, but yields a neutral solution. Mercury acts very rapidly, the metal being oxidised (compare Giles, *Chem. News*, 1867, **15**, 204; Borar, T., 1911, **99**, 1414).

C. H. D.

Atmospheric Corrosion of Commercial Sheet Iron. E. A. RICHARDSON and L. T. RICHARDSON (*Chem. News*, 1917, **115**, 62—65).—Two sets of specimens have been used for the comparative tests, one being in the condition as received, and the other annealed and then cleaned from scale by pickling in dilute sulphuric acid, washing and drying, and rubbing with emery. Ten similar specimens of each metal are used for the test, and are placed in a rack exposed to the atmosphere, in a place fairly free from acid fumes. A specimen is considered to have failed when it can be seen to be perforated when the rust is removed by tapping with a blunt object, the thickness of the sheets being in all cases 26 gauge.

The character of the coating of rust varies greatly with the composition of the steel. Bessemer and open-hearth steels form a loose, yellow rust, the other varieties forming a dark red, adherent deposit. The adherence is a maximum in the copper steels, which form a very dark, fine-grained rust. The period of resistance varies from about 350 days for mild steel in the given conditions to more than 1200 days for iron and steel containing copper, these specimens not having failed at the time of the report. The proportion of copper ranges from 0·181 to 0·268%. Charcoal iron and commercial pure iron resist better than mild steel, and the superior resistance of wrought iron is attributed to its greater purity rather than to the presence of slag. Copper has a greater effect on the resistance of steel than on that of iron.

C. H. D.

Some Problems of the Oxides of Iron. ROBERT B. SOSMAN (*J. Washington Acad. Sci.*, 1917, **7**, 55—72).—Ferrous oxide has never been obtained in a pure state, and from the analogy of iridium, it is possible that FeO may have a higher dissociation pressure than Fe_3O_4, which would explain the frequent presence

of metallic iron and the magnetic oxide in the products of oxidation or reduction. The presence of metallic iron in basic rocks in Greenland may be due to the dissociation of a complex ferrous silicate in this way. Ferrous and ferric oxides form a continuous series of solid solutions.

The magnetic properties of the iron oxides and the geological relations of the oxides are also discussed. C. H. D.

The System H_2O—Bi_2O_3—HCl **at 30°.** W. JACOBS (*Chem. Weekblad*, 1917, **14**, 208—212).—An investigation by the graphic method of systems made up of bismuth trioxide and aqueous solutions of hydrochloric acid. A. J. W.

Mineralogical Chemistry.

Oceanic Salt Deposits. J. D'ANS, with A. BERTSCH and A. GESSNER (*Zeitsch. Kali.*, 1915, **9**, 148—154, 161—168, 177—183, 193—200, 217—222, 229—236, 245—250, 261—270; from *Jahrb. Min.*, 1916, ii, Ref., 154—156).—Continuing the work of van't Hoff, the authors have (1) investigated anew the whole of the simple ternary and quaternary systems; (2) determined the isotherms for these systems at 0° and 55°, van't Hoff's having been determined at 25° and 83°; (3) investigated the range of existence of calcium sulphate. The complete investigation of the non-variant points is reserved to a later date. Microscopic methods were found to be of great assistance in the research. By means of tables and diagrams the new results are compared critically with those of earlier investigations.

The following systems are dealt with: (1) $KCl-NaCl-H_2O$; (2) $NaCl-MgCl_2-H_2O$; (3) $KCl-MgCl_2-H_2O$; (4) $NaCl-KCl-MgCl_2-H_2O$; (5) $Na_2SO_4-NaCl-H_2O$; (6) $K_2SO_4-KCl-H_2O$; (7) $Na_2SO_4-K_2SO_4-H_2O$; (8) the reciprocal salt pair, $K_2SO_4+2NaCl \rightleftarrows Na_2SO_4+2KCl$; (9) $MgSO_4-MgCl_2-H_2O$; (10) $Na_2SO_4-MgSO_4-H_2O$; (11) the reciprocal salt pair, $Na_2SO_4+MgCl_2 \rightleftarrows 2NaCl+MgSO_4$; (12) $K_2SO_4-MgSO_4-H_2O$; (13) the reciprocal salt pair, $K_2SO_4+MgCl_2 \rightleftarrows 2KCl+MgSO_4$; (14) $Na_2SO_4-K_2SO_4-MgSO_4-H_2O$.

In a sodium-free system containing the components K_2, Mg, SO_4, Cl_2, and H_2O it is found that kainite is not formed below about 13°, but can only exist in contact with the solution between 13° and 85°.

In the complete system of the chlorides and sulphates of sodium, potassium, and magnesium with water, solubility diagrams at 0° and 55° for complete saturation with sodium chloride have been obtained. The results are represented by means of the projection of a solid figure, the three co-ordinates being the quantities of

K_2, Mg, and SO_4 per 1000 mols. H_2O. The increase of solubility with solutions rich in magnesium chloride is clearly shown.

The conditions of formation of the calcium sulphate salts anhydrite, gypsum, glauberite, syngenite, pentacalcium sulphate, $K_2SO_4,5CaSO_4,H_2O$, and polyhalite were also determined. Experimental difficulties were encountered in the form of hysteresis effects, especially in the case of anhydrite. In the space diagrams given, the calcium salt fields are well shown for solutions saturated with sodium chloride.

The crystallisation of sea water at 0°, 25°, 55°, and 83° was studied, on the supposition that complete equilibrium was attained, and the results of these experiments are compared with the natural salt deposits. These deposits are considerably poorer in magnesium than would be expected from the experiments, and it is probable that magnesium chloride has been dissolved out. Probably the deposits were first formed at 25—30°, but there must subsequently have been a considerable rise of temperature.

E. H. R.

Identity of Hamlinite with Goyazite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1917, [iv], **43**, 163—164).—A tabulation of the characters, so far as determined, of goyazite from Brazil (Damour, 1884) and of hamlinite from Maine and Switzerland (Hidden and Penfield, 1890) suggests the identity of these minerals; or, at least, their essential difference remains to be proved. The material is a hydrous phosphate of aluminium and strontium crystallising in the rhombohedral system and belonging to the alunite–beudantite group of minerals.

L. J. S.

Two so-called Halloysites from Georgia and Alabama. P. A. VANDER MEULEN (*Amer. J. Sci.*, 1917, [iv], **43**, 140—144).—Analysis I is of a sedimentary clay, possessing the external characters of halloysite, and hitherto referred to that species, from Chattooga County, Georgia; and II of similar material from the Fort Paine chert formation in northern Alabama. They contain less water and more alumina and have a higher density than halloysite ($Al_2O_3,2SiO_2,2H_2O$ + aq.), and they are probably mixtures of kaolinite ($Al_2O_3,2SiO_2,2H_2O$) and gibbsite ($Al_2O_3,3H_2O$), containing respectively 21·32% and 4·83% of gibbsite. Minute, acicular crystals of gibbsite were detected on crevices in the Georgia clay. The presence of gibbsite in greater amount in I is also suggested by the fact that more water is lost at 300° than from II, and that dilute sulphuric acid extracts more alumina:

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	Na_2O.	H_2O 108°.	H_2O >108°.	Total.	Sp. gr.
I.	35·82	44·38	trace	trace	1·18	1·61	16·63	99·62	2·497
II.	43·30	39·94	trace	0·21	0·25	1·28	15·04	100·02	2·441
III.	43·18	39·21	0·15	trace	0·08	3·39	14·23	100·24	2·460

Analysis III is of a similar clay from Grubb mines, near Roanoke, Virginia.

L. J. S.

The Sodium Potassium Nephelites. N. L. Bowen (*Amer. J. Sci.*, 1917, [iv], **43**, 115—132).—The results are given of an experimental investigation of the binary system $NaAlSiO_4$–$KAlSiO_4$. The sodium compound occurs in two enantiomorphous forms, nephelite and carnegeite, with an inversion point at 1248°. The higher temperature form, carnegeite, melts at 1526°. The potassium compound also shows two forms: kaliophilite, isomorphous with nephelite, and an orthorhombic form with twinning, like that of aragonite. The orthorhombic form is apparently stable at temperatures above 1540° and melts at about 1800°. The potassium compound has a eutectic with carnegeite at 1404°. With nephelite it forms an unbroken series of solid solutions. It is concluded, therefore, that $NaAlSiO_4$ and $KAlSiO_4$ are the fundamental molecules of natural nephelite. The presence of calcium and of excess of silica in the natural mineral is explained by the solid solution of the albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) molecules (compare A., 1912, ii, 176, 774). L. J. S.

An Application of Polydimensional Geometry to Chemico-mineralogical Problems. The Composition of Tourmaline. H. E. Boeke (*Jahrb. Min.*, 1916, ii, 109—148).—For the quantitative graphical representation of systems of more than four components the author advocates the use of geometrical conceptions in four or more dimensions. The simpler properties of four-dimensional space are considered in some detail, and the method is then applied to a study of the composition of tourmaline.

The theories which have been advanced to explain the composition of the tourmalines fall into two groups: (1) those which postulate two or three distinct molecules, which, mixed in suitable proportions, will form any of the known varieties of tourmaline; (2) those which start from one or more fundamental forms in which replacement of certain chemical elements or groups in equivalent proportions can take place. After a critical examination of old analyses and of fifty-four new trustworthy analyses of tourmalines the author comes to the following conclusions: The relative amounts of silica and boric acid show a constant ratio, $SiO_2:B_2O_3 = 4:1$. If the mono-, bi-, and ter-valent metals be replaced by hydrogen equivalents, the ratio total hydrogen : Si varies between 56 : 12 and 72 : 12, but is generally 20 : 4. It appears to be very probable that the general formula $H_{20}Si_4B_2O_{21}$ first suggested by Penfield and Foote, is correct.

For the graphic representation of tourmaline the author distinguishes five components: *a*, H_2O; *b*, R_2O ($=Na_2O+Li_2O+K_2O$); *c*, RO ($=MgO+CaO+FeO+MnO$); *d*, R_2O_3 ($=Al_2O_3+Fe_2O_3+Ti_2O_3$); *e*, $SiO_2+B_2O_3$.

From an origin *E*, representing the constant component ($SiO_2+B_2O_3$), four axes all at right angles to one another are drawn, each of length = 100, ending in the points *A*, *B*, *C*, *D*, representing the pure components H_2O, R_2O, RO, and R_2O_3. The five points *A* to *E* describe a four-dimensional pentahedron, rectangular at *E*, bounded by ten edges, ten planes, and five three-dimensional spaces. The

composition of any tourmaline is represented by a point within this pentahedron. For the examination of the mutual relationships of the four variable components in pairs, six plane projections are necessary. It is found that the points representing the composition of tourmaline in four-dimensional space S_4 do not belong to one three-dimensional space S_3, nor to a single plane S_2. If the formula of Penfield and Foote were strictly correct, all tourmaline points should fall within one tetrahedron in S_3. It remains to be seen whether the departures from the formula $H_{20}Si_4B_2O_{21}$ are to be attributed to analytical errors or to the incorrectness of the formula. E. H. R.

Analytical Chemistry.

Graph for Correcting Volumes of Gases to 0° and 700 mm. MARCEL RIGOTARD (*Ann. Chim. anal.*, 1917, **22**, 21—23).—The graph is constructed from the correction factors given in the following table:

	710 mm.	720 mm.	730 mm.	740 mm.	750 mm.	760 mm.	770 mm.
10°	0·9013	0·9138	0·9266	0·9393	0·9519	0·9647	0·9775
15°	0·8857	0·8981	0·9105	0·9230	0·9354	0·9480	0·9605
20°	0·8706	0·8828	0·8950	0·9073	0·9195	0·9318	0·9441
25°	0·8560	0·8680	0·8801	0·8922	0·9042	0·9162	0·9283

For example, the volume of a gas measured at 20°/740 mm. is multiplied by 0·9073 to obtain its volume at 0°/760 mm.

W. P. S.

Urotropine [Hexamethylenetetramine] as a Microchemical Reagent. R. VIVARIO and M. WAGENAAR (*Pharm. Weekblad*, 1917, **54**, 157—161).—A description of crystalline derivatives formed by urotropine with metallic salts, with a summary of the literature.

A. J. W.

Lunge's Method for the Rapid Estimation of Sulphur in Roasted Ores. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1917, **22**, 26—27).—A quantity of 3·2 grams of the powdered substance is mixed with 2 grams of sodium hydrogen carbonate and heated gently for ten minutes, then for twenty minutes at a dull red heat. After cooling, the mixture is treated with water, boiled, the solution filtered, the insoluble portion washed with boiling water, and the filtrate titrated with $N/1$-hydrochloric acid. Two grams of sodium hydrogen carbonate are also titrated under similar conditions; the difference in the quantities of hydrochloric acid used for the two titrations is divided by 2 to obtain the percentage quantity of sulphur in the sample. The results obtained by the method are sufficiently trustworthy for practical purposes.

W. P. S.

Benedict's Method for the Estimation of Total Sulphur in Urine. MAURICE H. GIVENS (*J. Biol. Chem.*, 1917, **29**, 15—17. Compare Benedict, A., 1909, ii, 827; 1911, ii, 330).—The decrepitation which sometimes occurs during the oxidation of the sulphur compounds with copper nitrate is avoided if the urine is mixed with the Benedict reagent and slowly evaporated to dryness over a hot plate. The residue is then directly ignited over a Bunsen burner. H. W. B.

Lunge's Method for the Rapid Estimation of Arsenic in Sulphuric Acid. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1917, **22**, 24—25).—This method was found to be trustworthy; the results tend to be slightly too low, but a correcting factor may be found and applied in practice. Twenty c.c. of the sulphuric acid are diluted to about 50 c.c. and treated for ten minutes with a current of sulphur dioxide; the mixture is then heated, and a current of carbon dioxide is passed through it until all sulphur dioxide has been expelled. After further dilution, the solution is neutralised with sodium hydrogen carbonate and titrated with $N/20$-iodine solution. W. P. S.

A Colloido-chemical Phenomenon as Indicator in Quantitative Analysis. J. F. SACHER (*Koll. Zeitsch.*, 1916, **19**, 276—277).—In the estimation of lead by titration with a solution of ammonium molybdate, the supernatant liquid is turbid so long as the reaction is incomplete, but this turbidity disappears suddenly at the end-point. The turbidity is due to colloidal lead molybdate, and the coagulation of this serves to indicate the end-point.

In practice, the solution of lead, acidified with acetic acid, is heated at 70—80°, and the progress of the titration is determined by removing a drop of the solution and observing its optical condition. The end-point is independent of the quantity of acetic acid present, and the method is to be preferred to the older procedure in which tannin is used as indicator. H. M. D.

[Estimation of Copper in Blood of Molluscs and Crustacea.] CH. DHÉRÉ (*J. Physiol. Path.-gen.*, 1916, **16**, 985—997).—See this vol., i, 236.

Estimation of Manganese in High-speed Steels. C. T. NESBITT (*Chem. News*, 1917, **115**, 61—62).—On account of the difficulty of obtaining bromine, methods of analysis which do not require the use of bromine are to be preferred for high-speed steels. In the basic acetate method, bromine may be replaced by ammonium persulphate when that salt is obtainable in a pure state, but with most of the persulphate now supplied the results are always high. Potassium chlorate and hydrochloric acid are not satisfactory. Hydrogen peroxide or sodium peroxide also yields a precipitate which readily redissolves if any large excess of ammonium salts is present. The zinc oxide and cadmium carbonate methods give lower results than the standard gravimetric method.

Oxidation with bismuthate is to be preferred, and the following procedure must be adopted for high-speed steels. 1·1 Grams of steel drillings are dissolved in 12 c.c. of concentrated hydrochloric acid and evaporated to a syrup with 5 c.c. of concentrated nitric acid. After adding exactly 7 c.c. of concentrated sulphuric acid and rinsing down with water, the mixture is heated strongly for fifteen minutes, cooled, mixed with 30 c.c. of nitric acid (D 1·2) and 20 c.c. of water, boiled, and filtered through pulp. The precipitated tungstic oxide is washed, and the filtrate and washings are mixed with 15 c.c. of nitric acid to bring up the strength to D 1·2, boiled, oxidised with a little bismuthate, and cleared with 10 c.c. of sulphurous acid. After boiling off sulphur dioxide, the liquid is cooled, oxidised with 0·2 gram of bismuthate, shaken for two or three minutes, and filtered through asbestos. The residue is washed with 3% nitric acid, and titrated with ferrous sulphate and potassium permanganate. There is a transient pink coloration shortly before the true end-point. The heating to strong fuming with sulphuric acid and addition of sulphurous acid are necessary to remove chromium. Solution in hydrochloric acid and subsequent addition of sulphuric acid is much more rapid than direct solution in sulphuric acid. C. H. D.

Estimation of Tungsten and Silicon in Tungsten Steel. C. F. van Duin (*Chem. Weekblad*, 1917, **14**, 169—173).—The author finds that Ziegler's method for the estimation of tungsten in tungsten steel is untrustworthy, and that Zinberg's method gives inaccurate results for tungsten and too high results for silicon. A. J. W.

Analysis of Babbit Metal and Alloys of Tin, Antimony, Lead, and Copper. E. W. Hagmaier (*Met. & Chem. Eng.*, 1917, **16**, 84—85; from *J. Soc. Chem. Ind.*, 1917, **36**, 221).—The following process is recommended: *Antimony.*—1 Gram of filings is heated with water (10 c.c.) and sulphuric acid (25 c.c.) until no black particles remain. The cooled solution is diluted with water (100 c.c.) and hydrochloric acid (10 c.c.), boiled for ten minutes to expel sulphurous fumes, and titrated with potassium permanganate after being cooled and further diluted with water (100 c.c.). *Tin.*—The sample (0·5 gram) is dissolved in hydrochloric acid (with potassium chlorate if necessary), and the tin estimated by titration with $N/10$-iodine solution after reduction with soft iron and hydrochloric acid. *Lead.*—Solution is effected by dilute nitric acid in the presence of a large excess of tartaric acid. Sulphuric acid is then added, and the solution boiled sufficiently to expel all nitrous fumes, but without charring the tartaric acid; the lead sulphate is subsequently collected, dissolved in ammonium acetate solution, and the lead reprecipitated and weighed as chromate. *Copper.*—Solution is effected as in the preceding case, and the filtrate from the lead sulphate is further acidified with hydrochloric acid and heated with pure aluminium. The precipitated

copper is collected and redissolved in dilute nitric acid for determination by the electrolytic or iodide method. H. W.

Biochemical Reactions for Distinguishing between the Three Isomeric Dihydroxybenzenes: Catechol, Quinol, and Resorcinol. JULES WOLFF (*Compt. rend. Soc. Biol.*, 1916; from *J. Pharm. Chim.*, 1917, [vii], **15**, 94).—An intense blue coloration is obtained when 2 c.c. of a 0·1% catechol solution are treated with 2 drops of a glycerol extract of *Russula delica* (or other fungus rich in laccase), 5 drops of 3% potassium iodide solution containing 2% of soluble starch, and 3 drops of 5% acetic acid. The reaction is not given by quinol, but in this case a blue coloration develops gradually when $N/1$-sulphuric acid is used in place of the acetic acid. Resorcinol does not give a coloration either in the presence of acetic acid or of sulphuric acid. W. P. S.

A New Reaction for the Water-soluble, Active Glucoside from Digitalis Leaves. F. WRATSCHKO (*Zeitsch. allg. Österr., Apoth.-Ver.*, 1916, **54**, 263; from *Chem. Zentr.*, 1916, ii, 849).—A few c.c. of orcinol–hydrochloric acid reagent (0·2 gram of orcinol, 100 c.c. of concentrated hydrochloric acid, 4 drops of ferric chloride, solution) are heated to boiling, a few drops of the liquid under investigation are added, and the mixture is shaken. A green to blue colour develops, or, at greater concentration, a dark precipitate is formed. The solution is treated with an equal volume of water and shaken with amyl alcohol, whereby the latter is coloured green to dark blue; in the course of a few hours, this colour changes to a more stable lilac to carmine-red tint. The intensity of the colour is dependent on the digoside content of the liquid under investigation. The reaction is very sensitive. In the rare case in which the presence of free pentoses is considered possible, a preliminary extraction of the active glucoside with chloroform is necessary; the chloroform is removed, the residue dissolved in alcohol, and the solution tested as described. *Strophanthus* tincture and the aqueous and chloroform extracts of *Strophanthus* seeds also show this reaction. H. W.

Detection of Hydrocyanic Acid. GEORGE W. ANDERSON (*J. Soc. Chem. Ind.*, 1917, **36**, 195—196).—The sensitiveness of various methods for the detection of hydrocyanic acid has been investigated. For this purpose, solutions of potassium cyanide (98·5%) were prepared ranging in strength from 0·00001% to 0·1%, and therefore containing 0·00000393 to 0·0393 gram of cyanogen in 100 c.c. For each test, 10 c.c. of solution were employed, and all the reagents were examined and found to be pure.

Detection of hydrocyanic acid as silver cyanide.—A precipitate of silver cyanide is formed when silver nitrate is added to a solution of hydrocyanic acid or an alkali cyanide in presence of nitric acid when the dilution does not exceel 0·00039 gram of cyanogen per 10 c.c. In more dilute solution an opalescence is produced. The limit of sensitiveness is reached in a 0·0001% solution. Supersaturation of the solution with ammonia before addition of silver

nitrate and nitric acid does not lead to better results. Excess of acid must be avoided, but excess of silver nitrate is necessary. *Detection as Prussian-blue.*—The reaction was found to fail at concentrations lower than 0·001%; at this concentration, the coloration only appeared after half to one hour. This result is due to incomplete conversion of cyanide into ferrocyanide, since the presence of the latter can be detected at dilutions corresponding with 0·000024 gram of cyanogen. *Detection as thiocyanate.*—The tests were carried out according to the directions of Link and Möckel, and showed that when 0·00039 gram of cyanogen (0·01%) or more is present in 10 c.c., a deep red colour appeared, which became lighter with increasing dilution, finally showing a faint orange tint. The limit of sensitiveness is reached with a 0·0001% solution (0·0000039 gram of cyanogen per 10 c.c.). *Detection by means of picric acid.*—A series of tests showed the sensitiveness of this reaction to be limited, and, moreover, the same coloration may be produced by impurities in the acid or alkali or by reducing substances (sugar, sulphur dioxide, etc.). *Detection by means of guaiacol.*—This test, known as the Schönbein-Pagenstecher reaction, is the most sensitive for the detection of hydrocyanic acid. Adopting the modification suggested by Maisel, the author has been able to detect as little as 0·00000039 gram of cyanogen in 10 c.c. (0·00001% potassium cyanide). The reaction, however, is easily disturbed by the presence of alien substances, such as ammonia or cigar smoke.

The author draws the conclusion that, although the Schönbein-Pagenstecher method is the most sensitive, it can only be used as a preliminary test in conjunction with use of the other reactions, for example, the Prussian-blue or silver cyanide test, of which the latter is often preferred in forensic chemistry. This test, however, generally requires a double distillation of the original solution under examination in order to obtain a distillate free from chlorine. The Prussian-blue test will suffice for ordinary purposes, whilst the thiocyanate reaction may be useful in special cases. The picric acid reaction cannot be recommended. H. W.

Estimation of Hydrocyanic Acid in Sorghum vulgare. J. J. Willaman (*J. Biol. Chem.*, 1917, **29**, 25—36).—See this vol., i, 245.

Estimation of Unsaponifiable Matter in Oils and Fats. J. Davidsohn (*Chemische Umschau Fett. Harz-Ind.*, 1916, **23**, 130—131; from *Chem. Zentr.*, 1916, ii, 1076).—Five grams of fat are saponified with $N/2$-alcoholic potassium hydroxide (50 c.c.), and the solution is evaporated nearly to dryness. The residue is dissolved in water and twice extracted with ether. The ethereal solution is distilled and evaporated to dryness after addition of a little alcohol. The residue is weighed, warmed with water (50 c.c.), and titrated with $N/10$-acid in the presence of methyl-orange. The weight of soap thus found is deducted from that of the extract.

H. W.

Method for Accurately Estimating Arginine in Proteins. B. C. P. JANSEN (*Chem. Weekblad*, 1917, **14**, 125—129).—Arginine can be estimated quantitatively in proteins by the action of arginase and urease on the hydrolysed product after elimination of the ammonia. The arginase decomposes the arginine, with formation of an equimolecular proportion of urea, which is converted by the urease into ammonium carbonate. A. J. W.

Factors Involving the Accuracy of Creatinine Estimations in Human Blood. ALEXANDER O. GETTLER [with RUTH OPPENHEIMER] (*J. Biol. Chem.*, 1917, **29**, 47—56. Compare Folin and Doisy, this vol., ii, 159).—The authors point out that oxalates have a strong bleaching action on the picramic acid colour, and therefore only the requisite amount of oxalate should be used to prevent the coagulation of the sample of blood. The colour produced by picric acid and creatinine in the presence of alkali is only due in part to the creatinine, and it is therefore inaccurate to reckon the total colour produced as due to this substance. The authors give a table, from which the actual amount of creatinine can be determined from any intensity of colour produced under standard conditions.

The amount of creatinine in normal blood ranges from 0·1 to 0·4 mg. in 100 c.c. The values of 1 to 2 mg. in 100 c.c. given by Folin and Denis (A., 1914, i, 764) are much too high. H. W. B.

Tests for certain Narcotic and Anæsthetic Drugs. E. H. HANKIN (*Indian J. Med. Research*, 1916, **4**, 237—255).—Colour reactions of a large number of alkaloids, narcotic substances, etc., are recorded, and more particularly those given by cycloform, β-eucaine, orthoform, nirvanine, anæsthesine, novocaine, holccaine, acoine, stovaine, and alypine. Nitric acid gives a yellow coloration with cycloform, reddish-brown with holocaine, and brownish-black with acoine. Alypine, cocaine, tropacocaine, and α-eucaine yield red crystals when their solutions are mixed with alum solution and the mixtures added to potassium permanganate crystals on a microscope slide; β-eucaine and stovaine form red, oily drops with this reagent. Most of the substances give a white precipitate when treated with Fehling's solution. Reactions with sulphuric acid and potassium iodate, sulphuric acid and hexamethylenetetramine, and with bromine are also described. W. P. S.

General and Physical Chemistry.

The Refractive Power and the Specific Refraction of Dispersoids. GEORGE WIEGNER (*Kolloid Zeitsch.*, 1917, **20**, 7—19).—A theoretical discussion of the various formulæ which have been suggested as affording a measure of the refractive power of a liquid. The refractivity R of the disperse phase in colloidal solutions of arsenious sulphide, ferric hydroxide, tannin, and silicic acid is calculated from the refractive indices and densities of solutions of variable concentration on the assumption that $R = n - 1/d$ or $= n^2 - 1/(n^2 + 2)d$, and that the mixture rule is applicable to the refractivity of the colloidal system. The ordinary mixture formula involving R is transformed so as to express the refractive index and specific volume of the colloidal system in terms of the corresponding quantities for the disperse phase and the dispersive medium.

H. M. D.

The Periodic System of the Elements and Spectrum Analysis. VIKTOR KUTTER (*Physikal. Zeitsch.*, 1917, **18**, 16—17). —The metallic elements may be roughly divided into four groups according to the facility with which their spectra may be obtained. The elements of the first group give a satisfactory spectrum in the Bunsen flame. In the case of elements belonging to the second group the flame spectrum is only feebly developed, but spark discharge gives a good spectrum. The elements of the third and fourth groups give no spectrum in the Bunsen flame, but are distinguished by the fact that elements in the third group yield a spectrum with ordinary spark discharge, whilst those in the fourth group require condensed spark discharge.

The grouping of the elements on this basis gives some indication of their relative volatilities, and attention is directed to the circumstance that this volatility appears to be a periodic function of the atomic weight.

H. M. D.

The Arc Spectrum of Samarium. JOSEF MARIA EDER (*Sitzungsber. K. Akad. Wiss. Wien*, II., A., **125**; from *Chem. Zentr.*, 1917, i, 55. Compare this vol., ii, 1).—The variations in the wave-length tables of samarium when different specimens are used make it appear doubtful if the substance remains uniform after fractional separation from europium. Re-examination of 1046 lines of the arc spectrum shows samarium to be a spectroscopically well-characterised element which may contain small amounts of a possibly new, unknown element. Samarium itself is probably the neighbouring element to europium in the periodic system. With small dispersion the samarium spectrum appears to consist of strong lines which, at greater dispersion, are found to be resolved into very many lines of similar brightness. H. W.

Solvent Effect and Beer's Law. ALFRED WALTER STEWART and ROBERT WRIGHT (T., 1917, **111**, 183—187).—Previous observations on the absorption spectra of aqueous and ethyl-alcoholic solutions of iodine (A., 1911, ii, 1043) have shown that Beer's law does not represent the variation of the absorption with the concentration in either of these solvents. In aqueous solution the absorption increases with the concentration, whereas the converse holds for alcoholic solutions.

Further experiments with iodine in other solvents show that the absorption increases with concentration in chloroform and carbon tetrachloride, but decreases with increasing concentration in ethyl ether and methyl acetate. Light petroleum resembles the oxygenated solvents, but its influence is only slight. It is suggested that the presence of oxygen in the solvent is mainly responsible for the observed differences. H. M. D.

The Absorption Spectrum of Nitric Acid Vapour. KONR. SCHAEFER [with ST. DEICHSEL) (*Zeitsch. anorg. Chem.*, 1916, **98**, 70—76. Compare this vol., ii, 61).—On account of the rapid decomposition of nitric acid vapour by light, it is necessary to maintain a stream of the vapour through the absorption tube during the photographing of the spectrum. The absorption tube is electrically heated at 130°, the constant boiling acid being used. There is no absorption band, the curve being very similar to that given by a liquid 98·7% acid. The NO_3 group in the vapour is therefore in a similar state to that in the alkyl nitrates and in the concentrated acid. C. H. D.

Optical Investigation of Mixtures of Nitric and Sulphuric Acids. KONR. SCHAEFER [with H. NIGGEMANN] (*Zeitsch. anorg. Chem.*, 1916, **98**, 77—85. Compare this vol., ii, 61).—Pure 95% sulphuric acid is optically transparent, but the addition of sulphur trioxide to bring up the strength to 100% causes absorption. The trioxide is rendered optically clear by redistillation. The two acids are mixed in a modified Beckmann apparatus, but the heat developed is liable to cause decomposition of the nitric acid, so that it is better to add finely powdered potassium nitrate to the sulphuric acid. The absorption limit of 0·2*N*-nitric acid is displaced towards the ultra-violet even by 20% sulphuric acid, the absorption curve being flattened at the same time, and this effect increases with increasing concentration of sulphuric acid. The acid is considered to act as a dehydrating agent, displacing the equilibrium between the two modifications of the NO_3 group. C. H. D.

Researches on the Absorption Spectra of Metal Ammines. II. (A.) Absorption Spectra and Electrolytic Conductivity of Aqueous Solutions of Co-ordination Polymeric Nitroammine-cobalt Complexes. (B.) Absorption Spectra of Aqueous Solutions of Polynuclear Ammine-cobalt Complexes. YUJI SHIBATA [with K. MATSUNO] (*J. Coll. Sci. Tokyo*, 1916, **37**, 1—31).—(*A.*) In a previous paper (A., 1916, ii, 277), the absorption spectra of complex cobaltammines have been studied,

the complex anions or cations being combined with the ordinary inorganic and simple cations or anions. The investigation has now been extended to the case of salts where both the anions and cations are complex, the salts investigated being the following co-ordination polymerides of the general formula

$$n[Co(NH_3)_3(NO_2)_3]:\ [NO_2\cdot Co(NH_3)_5][(NO_2)_4Co(NH_3)_2]_2,$$

$$\left[\begin{matrix}(1)NO_2\\(2)NO_2\end{matrix}Co(NH_3)_4\right][(NO_2)_4Co(NH_3)_2],$$

$$\left[\begin{matrix}(1)NO_2\\(6)NO_2\end{matrix}Co(NH_3)_4\right][(NO_2)_4Co(NH_3)_2],$$

$$[NO_2\cdot Co(NH_3)_5]_3[Co(ONO)_6]_2,$$

$$\left[\begin{matrix}(1)NO_2\\(2)NO_2\end{matrix}Co(NH_3)_4\right]_3[Co(ONO)_6],\quad \left[\begin{matrix}(1)NO_2\\(6)NO_2\end{matrix}Co(NH_3)_4\right][Co(ONO)_6].$$

The absorption spectra were examined in solutions varying in concentration from 1/100 to 1/10,000 equivalent. All the solutions were stable, and the absorption conformed to Beer's law.

The absorption spectra show that the above six salts can be divided into two classes, the first class comprising the first three salts and the second class the last three salts. The salts in the first class all show a characteristic absorption band (in the strict sense of the word it is not a band, since there is no maximum point of absorption) at a frequency of 2200, and two other absorption bands at frequencies of 3000 and 4000. The second band, frequency 3000, is common to all the nitro-ammine–cobalt complexes. The salts in the second class have two or three absorption bands, the first being at a frequency of 2100, the second at 3000, and the third, which exists in the case of

$$\left[\begin{matrix}(1)NO_2\\(6)NO_2\end{matrix}Co(NH_3)_4\right]_3[Co(ONO)_6]$$

only, at a frequency of 4000. In general, it may be said that the absorption spectra of the above six polymerides containing complex anions and cations are additive, except in the case of the characteristic band peculiar to the first three. Investigation of the electrolytic conductivity of these salts showed, by comparison with the conductivities of complex salts with either the anion or cation of a simple character, that it was normal in every case. The characteristic absorption band is explained, in the light of Stark's theories, by the presence of a "loosened" valency electron in the first three salts.

(*B*.) The absorption spectra of the following polynuclear complexes have been studied:

$$\left[Co\left\{\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right\}_3\right]Cl_6,\quad \left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]Cl_4,$$

$$\left[(NH_3)_4Co\begin{matrix}NH_2\\OH\end{matrix}Co(NH_3)_4\right]Cl_4,4H_2O,$$

$$\left[(NH_3)_4Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_3,$$

$$\left[(NH_3)_4Co\begin{matrix}H_2O\\NH_2\\Cl\end{matrix}Co(NH_3)_4\right]Cl_4.$$

The dilutions varied from $N/100$ to $N/10,000$, except with the fourth salt, where they varied from $N/400$ to $N/4000$. Satisfactory results could not be obtained from the pure aqueous solutions, owing to gradual hydrolysis with the separation of cobalt hydroxide. The acid solutions, acidified with the corresponding mineral acid, were stable and conformed to Beer's law.

Each of the salts gave, in acid solution, practically the same absorption spectra, showing two absorption bands at frequencies of approximately 2000 and 3400—3500 respectively. This is ascribed to the fact that the cobalt complexes in the above salts, if one neglects the bridged linkings, are the same. The bridged linkings are very weak, as shown by the ready hydrolysis of the salts, and have no effect on the absorption of light. T. S. P.

Absorption of the Ultra-violet Rays by some Chloro-derivatives of Ethane, Ethylene, and Acetylene. G. MASSOL and A. FAUCON (*Compt. rend.*, 1917, **164**, 308—310).—An examination of the ultra-violet absorption spectra of hexachloroethane, tetrachloroethylene, *s*-tetrachloroethane, and acetylene in alcoholic solution. Hexachloroethane and *s*-tetrachloroethane have practically the same transparency for the ultra-violet rays. Tetrachloroethylene is much less transparent than these, and this is attributed to the fact that it is an unsaturated compound. None of these compounds shows the broad band characteristic of chlorine, the absorption being, in all cases, unilateral. Neither of the unsaturated compounds tetrachloroethylene or acetylene gives any special band. The limits of transmission of the ultra-violet rays by alcoholic solutions of the above compounds, of varying thickness, are tabulated. W. G.

Spectrochemistry of Benzene Derivatives and Cinnamic Esters. K. VON AUWERS (*Annalen*, 1917, **413**, 253—309).—See this vol., i, 266.

The Rotatory Power of Liquid Crystals. PAUL GAUBERT (*Compt. rend.*, 1917, **164**, 405—406. Compare Vorländer and Huth, A., 1911, ii, 165).—The author has used a new method for the measurement of the rotatory power of liquid crystals by superimposing on such a preparation a substance having a rotatory power, and determining in monochromatic light the displacement of the arms of the black cross obtained with Nicol prisms. The rotatory power, which is at first low, increases as the wave-length of the reflected colour increases. For each kind of rays, the substance is at first lævorotatory and then dextrorotatory. In some cases this change, in sense of the rotation, occurs just at the moment when the preparation reflects the rays. At this phase, one of the two circular rays is absorbed, and there is, consequently, no rotatory power for the colour considered, but when the tint passes towards the red, the rotatory power reappears in the inverse sense and goes on increasing. W. G.

The Action of Penetrating Radium Rays on Colloids. II. ALBERT FERNAU and WOLFGANG PAULI (*Kolloid Zeitsch.*, 1917, **20**, 20—33. Compare A., 1915, ii, 722).—In the further investigation of the action of penetrating radiation on inorganic colloids, experiments have been made with colloidal solutions of ceric hydroxide prepared by dialysis of a solution of ceric ammonium nitrate.

These colloidal solutions change in a marked manner with time, the ageing being accompanied by a diminution in viscosity, a gradual loss of the faculty to gelatinise, and by a diminution in the sensitiveness towards electrolytes. The change is irreversible, and is accelerated by rise of temperature. It is supposed that the ageing is due to the gradual dehydration of the sol particles.

The ageing of ceric hydroxide sols is very largely modified under the influence of β- or γ-rays from radium. The first effect consists in an accelerated rate of diminution of the viscosity, but this effect is succeeded by a second, in which the viscosity of the sol increases to a value very large in comparison with that of the freshly dialysed sol. The progress of the second stage is not dependent on the continued exposure of the sol to the action of the active rays, for if the exposure is made intermittent, it is found that the course of the viscosity–time curve is quite unchanged. A further curious effect is observed when the source of the radiation is removed before the end of the first stage in the ageing process. In these circumstances, the second stage in the ageing process sets in, and the viscosity of the sol increases very considerably, attains a maximum value, and subsequently decreases almost as rapidly as it increased before the attainment of the maximum. The jelly obtained when the radiation is allowed to act sufficiently long appears to be perfectly stable.

Similar changes in the viscosity are produced by the addition of electrolytes, although the effects are readily distinguishable. On the addition of a quantity of an electrolyte, which is not sufficient to produce coagulation, there is an immediate drop in the viscosity of the sol, and this is then succeeded by a gradual increase in the viscosity, the final result being a solid jelly. If the quantity of added electrolyte is smaller, the initial diminution in the viscosity is followed by an increase to a maximum, and thereafter the viscosity sinks slowly. The viscosity–time curve is thus very similar to that which represents the changes occurring after the ceric hydroxide sol has been exposed for a short time to the action of β- or γ-rays. There is, however, a marked difference between the two, in that the rising and falling branches on opposite sides of the maximum are much steeper in the case where the sol has been under the influence of the radiation. A further difference is found in the fact that the jelly produced by the action of electrolytes is unstable. It gradually becomes turbid, contracts, and sets free water.

Electrometric measurements of the chlorine ion concentration in sols to which sodium chloride has been added show that chlorine ions disappear at once when the electrolyte is added to the sol,

but that no further change occurs during the second stage of the ageing process.

Although, in a general way, the ageing of sols is supposed to be due to the gradual formation of larger colloidal particles by a process of aggregation, it is probable that the effects described by the authors are connected with changes in the degree of hydration. It is probable that ceric hydroxide and other metallic hydroxide sols are highly hydrated, and in this way differ from hydrophobic colloids, such as the metallic and the sulphide sols. Under the influence of electrolytes or β- or γ-rays, the electrical charge of the colloidal particles is neutralised, and this is accompanied by a diminution in the degree of hydration, and results in a lowering of the viscosity, gradual when the sol is subjected to β- or γ-rays and immediate when an electrolyte is added. The increase in viscosity in the second stage of the ageing process is then due to the aggregation of the electrically neutral particles, a process which takes place with a velocity comparable with that of crystallisation and similar processes.

The attainment of a maximum viscosity and the subsequent fall which is observed when the added electrolyte is very small in quantity or the time of exposure to the rays is comparatively brief is more difficult to explain, and the suggestion is put forward that this peptonisation is due to the action of electrically charged colloid particles which are enclosed by the jelly resulting from the aggregation of the electrically neutral particles. In support of this view, it has been found that ceric hydroxide jelly may be readily peptonised by the addition of the corresponding sol.

H. M. D.

Some Particular Cases of Current-potential Lines. II. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 768—778).—The considerations put forward in the previous paper (this vol., ii, 163) are applied to the electrolysis of solutions containing halogen ions with a silver anode. The most favourable conditions for the separation of halogen in the form of silver haloid at the anode with a minimum loss of silver by anodic dissolution are shown to be deducible from the theory put forward, and these conditions are for the most part those which have been found most satisfactory according to the empirical experiments which have been made by various observers. The fact that the accuracy with which the halogens can be estimated by this method increases with increase in the atomic weight of the halogen is due to the diminishing value of the ionic solubility product of the corresponding silver haloids.

The conditions favourable to the formation of insoluble metallic compounds by the anodic dissolution of the metal are also derived and found to agree with those indicated by practice.

The author's views are also applied to the electrolysis of solutions of complex salts, the alkali silver cyanide solution being specially considered, and it is shown that the conditions under which silver cyanide is deposited on the anode, thereby increasing

the resistance and reducing the current, may be deduced from the theory. To avoid this in practice, the current density must not exceed a certain value, which, of course, depends to some extent on the concentration of the solution. H. M. D.

The Surface Electric Double-layer of Solid and Liquid Bodies. J. FRENKEL (*Phil. Mag.*, 1917, [vi], **33**, 297—322).—A theoretical paper in which the origin of the electrical double-layer at the surface of solids and liquids is discussed.

It is assumed that the atoms consist of positive nuclei with electrons rotating about them, and by considering the surface layer it is shown that this atomic model necessarily gives rise to an electric double-layer, with the negative electrification external to the positive in the case of all metallic substances.

The phenomena associated with the existence of this double-layer are examined, and it is shown that the intrinsic potentials of all metals are positive and of the same order of magnitude as the corresponding ionising potentials. The intrinsic potentials tend to increase with the valency of the metals. In the case of insulators, the intrinsic potential may be positive or negative, such substances being distinguished from conductors by the absence of free electrons. Contact electromotive forces, whether of metals or dielectrics, are shown to be due to differences in the intrinsic potentials.

The electric double-layer is supposed to afford an explanation of the phenomena of surface tension. On the assumption that the surface tension depends exclusively on the energy of the electric double-layer and not at all on cohesive forces, the author calculates the atomic radii and the intrinsic potentials for a number of metals. The values thus obtained vary from two to six volts and correspond more or less with the ordinary electrochemical series. In the case of the atomic radii, the values are approximately equal to those corresponding, on Bohr's theory, with stationary orbits of the second order.

The theory affords an explanation of the relatively low surface tension of non-conductors compared with that of the metals, and also of the state of stress which is usually defined in terms of the internal pressure. H. M. D.

The Effect of Rust on the Corrosion of Iron and Steel. JAMES ASTON (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 449—464).—Measurements of the current in cells containing tap water through which air is bubbled show the influence of rust in accelerating the further rusting of iron and steel. Wet rust is anodic to bare iron, whilst dry rust is cathodic. The current densities are comparable with those given by the couples iron–carbon or iron–copper. When both electrodes are coated with rust of similar character, there are always sufficient differences to cause a flow of current. Wet ferric hydroxide has a high resistance. The anodic effect produced by wet rust is also caused by other colloidal hydroxides, gelatin, gum, parchment, and filter

paper, the action being probably one of preventing access of oxygen. Ferroxyl tests confirm the results of current measurements. Dry rust behaves like fresh wet rust if immersed for a sufficient time in water. C. H. D.

The Theoretical Existence of a Second Critical Point. MAURICE PRUD'HOMME (*J. Chim. phys.*, 1916, **14**, 445—448).—Analysis of the van der Waals's equation leads the author to the conclusion that a second critical point is theoretically possible. The characteristics of this point are subjected to analysis. H. M. D.

Determination of Melting Points at Low Temperatures. ALFRED STOCK (*Ber.*, 1917, **50**, 156—158).—Two forms of a device are described by means of which the difficulty of determining a melting point with a non-transparent bath is overcome. It is therefore equally serviceable for low and high temperatures. It consists essentially of a thin-walled tube about 6 mm. wide and a glass rod about 2 mm. thick, elongated to act as a pointer. By suitable means a ring of the solid substance is deposited on the wall of the tube a short distance from the sealed end and the glass rod is rested on it. The melting point is taken when the upper end of the pointer is observed to sink. J. C. W.

The Tension of Saturated Vapour at Low Temperatures and the Chemical Constant. E. ARIÈS (*Compt. rend.*, 1917, **164**, 477—480. Compare *ibid.*, 1917, **164**, 343).—A mathematical paper, in which the author deduces for the value of the chemical constant $A=(Ke/R)^{m-1}$, where m is the ratio C/c of the two specific heats of perfect gases. W. G.

Computation and Measurement of the Complex Molecules of Certain Vapours according to the New Condensation Theory. L. ANDRÉN (*Ann. Physik*, 1917, [iv], **52**, 1—71).—The condensation of water, ethyl alcohol, and benzene vapour in admixture with air, carbon dioxide, and hydrogen has been examined by experiments with a modified Wilson expansion apparatus. The observations are interpreted in accordance with Lenard's theory (*Sitzungsber. Heidelberg Akad.*, 1914, 29).

According to older experiments, the condensation may give rise to a comparatively small number of droplets or to the formation of fog, and these phenomena require different degrees of expansion which are, however, characteristic for a particular vapour–gas mixture. The author's experiments, on the other hand, lead to the conclusion that the two types of condensation cannot be differentiated by any definite expansion values and that there is no evidence of any real discontinuity. It would therefore seem that the various types of condensation nuclei are not of uniform size, but that there is a more or less continuous variation in the dimensions of the nuclei in each particular group.

It has been further found that the largest condensation nuclei are the ions formed under the influence of terrestrial radiation. The number of these nuclei depends on the nature of the vapour

and of the admixed gas. According to the experiments with air, the number of such charged nuclei in 1 c.c. is about 900.

In addition to the above, the experiments show the existence of a relatively very small number of uncharged nuclei of large size which begin to be effective when the degree of supersaturation is five. It is probable that these nuclei are the result of chemical changes brought about by the highly penetrating terrestrial radiation. By far the greater number of the uncharged nuclei are of smaller dimensions. For the most part they consist of polymerised molecules of the vapour, which contain two or three simple molecules. The number of such polymerised molecules is calculated to be $1 \cdot 9 \times 10^{-11}\%$ for water, $2 \cdot 5 \times 10^{-11}\%$ for ethyl alcohol, and $0 \cdot 8 \times 10^{-11}\%$ for benzene. These correspond respectively with 110,000, 340,000, and 190,000 nuclei per c.c.

The nature and number of the uncharged nuclei thus depend on the chemical nature of the vapour, but are not appreciably affected by the admixed permanent gas.

When the vapour–gas mixtures are submitted to β- or γ-rays from a radium preparation, uncharged nuclei of greater dimensions are produced than those normally present. The number and size of these increase with the intensity of the radiation.

The experimental observations are said to be in complete agreement with Lenard's views of the nature of the condensation process. In particular, the results support the view that there is a certain degree of supersaturation for every vapour which will bring all the nuclei into action as condensation centres. H. M. D.

Steam Distillation. F. J. Tromp (*J. Soc. Chem. Ind.*, 1917, **36**, 276).—The author has had occasion to distil considerable quantities of aniline in steam, and finds that very rapid and efficient condensation of the distillates is secured when the tube from the distillation vessel is led into a tank of water which can be cooled by a suitable cooling coil. The distillate is syphoned off periodically. Once the air has been completely expelled from the distillation vessel and connexions, there appears to be practically no limit to the rate at which steam can be passed, and condensation is complete as long as the liquor in the tank is below its boiling point.

H. W.

Heats of Vaporisation and Maximum Vapour Pressures. A. Leduc (*Compt. rend.*, 1917, **164**, 494—497).—The author has calculated the values of the latent heat of vaporisation, L, from the Clapeyron-Thomson formula, $L = T/J(u' - u)dF/dT$, in the case of ether and benzene. Taking the values of Ramsay and Young (compare *Phil. Trans.*, 1887, **178**) for the maximum pressure of ether between 0° and 60°, the values calculated for L do not agree with the experimental values according to Winkelmann (compare A., 1880, 692). There is a better agreement in the case of benzene at 80°. W. G.

Atomic Volumes of Oxygen and the Halogens at the Critical Point. Gervaise Le Bas (*Chem. News*, 1917, **115**, 146—147).—A comparison of the atomic volumes of free and com-

bined oxygen at the critical temperatures of the various substances concerned shows that the volume is three times that of hydrogen with the exception of alcoholic oxygen, the atomic volume of which is twice that of hydrogen. The relative volume of the halogens compared with hydrogen are at the critical temperatures: fluorine, 2·3; chlorine, 6·0; bromine, 7·7; iodine, 10·4. H. M. D.

Internal Friction of Chlorinated Aliphatic Hydrocarbons. W. HERZ (*Zeitsch. Elektrochem.*, 1913, **23**, 24).—The author has calculated from the specific viscosity measurements previously published (Herz and Rathmann, A., 1913, ii, 835) the absolute viscosities (*C.G.S.*) and the specific volumes. The following values are obtained: *cis*-dichloroethylene, 25°, $\rho=0·003901$; *trans*-dichloroethylene, 25°, $\rho=0·004553$; 50°, $\rho=0·003690$; trichloroethylene, 25°, $\rho=0·005490$, $v=0·6878$; 50°, $\rho=0·004466$, $v=0·7078$; 75°, $\rho=0·003709$, $v=0·7288$; tetrachloroethylene, 25°, $\rho=0·008391$, $v=0·6219$; 50°, $\rho=0·006567$, $v=0·6380$; 75°, $\rho=0·005335$, $v=0·6551$; tetrachloroethane, 25°, $\rho=0·01614$, $v=0·6297$; 50°, $\rho=0·01118$, $v=0·6450$; 75°, $\rho=0·008185$, $v=0·6611$; pentachloroethane, 25°, $\rho=0·02171$, $v=0·5984$; 50°, $\rho=0·01482$, $v=0·6117$; 75°, $\rho=0·01060$, $v=0·6255$. From these values the Batschinsky function between fluidity and specific volume can be confirmed.

J. F. S.

A Method for the Determination of Dissociation Pressures of Sulphides and its Application to Covellite (CuS) **and Pyrites** (FeS_2). E. T. ALLEN and ROBERT H. LOMBARD (*Amer. J. Sci.*, 1917, [iv], **43**, 175—195).—The method described depends on the balancing of the dissociation pressure of the sulphide against the vapour pressure of sulphur at a known temperature. In the application of this method, the sulphide and sulphur are contained in bulbs at opposite ends of an evacuated combustion or quartz tube. This tube is heated by a pair of coaxial cylindrical furnaces which are attached to carriages, so that the two furnaces may be easily slipped over the experimental tube and brought tightly end to end when an experiment is to be made. The bulb containing the sulphide is heated in the one furnace at a measured temperature, and by trial the temperature is ascertained at which the vapour pressure of the free sulphur in the other bulb is equal to the dissociation pressure of the sulphide. To facilitate the carrying out of this determination, the heating of the sulphide furnace is arranged so that the temperature throughout is as uniform as possible, whilst the sulphur furnace is heated in such a way that the temperature rises continuously from the outside to the inside end. By moving the carriages it is thus possible to make a series of observations with the sulphur bulb at various temperatures. The gain or loss of sulphur by the sulphide may be determined by the appearance, by analysis, or by making use of some physical property.

The method has been applied in the measurement of the dissociation pressures of covellite and pyrites over a range of 1 mm. to 500 mm. The dissociation pressure of covellite was thus found to

increase from 1·5 mm. at 400° to 510 mm. at 490° and that of pyrites from 0·75 mm. at 575° to 518 mm. at 680°. An advantage of the method is that the equilibrium may be approached from above and below, and the observer is consequently not likely to be deceived by false equilibrium phenomena. It has the disadvantage of requiring a considerable time, and cannot be used when the dissociation pressure is much greater than atmospheric.

The method may be applied to compounds other than sulphides provided that there is only one volatile dissociation product which does not attack glass or quartz and condenses at accessible temperatures. It also affords a convenient means for synthesising dissociating compounds. H. M. D.

Diameter (of Molecules) and Solubility. W. HERZ (*Zeitsch. Elektrochem.*, 1913, **23**, 23—24).—Making use of the previously calculated molecular diameters of organic liquids (Herz, A., 1915, ii, 682), the author now examines the connexion between this quantity and the solubility of these liquids in water. It is shown that generally the solubility is greater the smaller the diameter. Thus at 18°, 100 grams of solution contain 25 grams of methyl acetate (diameter $=0·94 \times 10^{-8}$), 5 grams of methyl propionate (diameter $= 1·04 \times 10^{-8}$), and 1·7 grams of methyl butyrate (diameter $=1·16 \times 10^{-8}$). The same is found with isomeric substances, which, although possessing equal molecular weights, yet have different molecular diameters; for example, propionic acid is completely miscible with water, whilst methyl acetate dissolves to the extent of 25 grams in 100 grams of the saturated solution. The diameters are: propionic acid, $0·63 \times 10^{-8}$; methyl acetate, $0·94 \times 10^{-8}$. This relationship is, however, not absolute, and can be entirely altered by specific chemical properties. J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 816—824. Compare this vol., ii, 132, 169).—A further discussion of the possible number of types of pressure–temperature diagrams, in which it is shown that although three types may be, in general, distinguished, the number is increased to four provided that two indifferent phases occur in the invariant point. Similarly, quaternary systems are generally characterised by four possible types of pressure–temperature diagrams, but in case there are two indifferent phases in the invariant point, the number of such types increases to twelve. The types in question are symbolically represented and divided into three groups.
H. M. D.

Four-component Systems. H. E. BOEKE (*Zeitsch. anorg. Chem.*, 1916, **98**, 203—222).—A general theoretical paper on the process of crystallisation in four-component systems, based on the tetrahedral representation of such systems, with special reference to the case of magmas. C. H. D.

Studies of the Carbonates. II. Hydrolysis of Sodium Carbonate and Sodium Hydrogen Carbonate and the Ionisation Constants of Carbonic Acid. CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD (T., 1917, **111**, 138—158).—The uncertainty attaching to previous determinations of the constant characteristic of the second stage in the ionisation of carbonic acid is probably due, for the most part, to errors involved in the assumptions made with respect to the degree of ionisation of sodium hydrogen carbonate and sodium carbonate. The difficulties incidental to the determination are discussed, and a new method is described which avoids the assumptions which have been made in earlier attempts to obtain the value of this constant.

If k_2 and k_3 are the first and second ionisation constants of carbonic acid, k_w the "constant" for water, α and β the degrees of ionisation of sodium hydrogen carbonate and sodium carbonate respectively, k_c the apparent value of the ratio

$$C^2_{NaHCO_3}/C_{Na_2CO_3}\,.\,[H_2CO_3],$$

and k_d the apparent value of $C_{NaHCO_3}\,.\,[OH']/C_{Na_2CO_3}$, then $k_c = k_2\beta/k_3\alpha^2$ and $k_d = k_w\beta/k_3\alpha$. From experiments with dilute solutions of sodium carbonate (+hydrogen carbonate) in equilibrium with atmospheric carbon dioxide, in which the carbonate and hydrogen carbonate concentrations were determined by titration and the hydrogen ion concentration by hydrolysis of ethyl acetate, k_c and k_d have been determined. Since k_2 and k_w are known, the value of α may be got from the two previous equations by eliminating k_3, when $\alpha = k_2k_d/k_wk_c$. It is thus found that the degree of ionisation of sodium hydrogen carbonate is very nearly the same as that of sodium acetate.

The value of k_c increases with the dilution, and its maximum value is taken to represent k_2/k_3, from which β may be calculated by means of the equation $\beta = k_c\alpha^2/k_2/k_3$. The value of β may be represented by the empirical formula $\beta = 1{\cdot}104 - 0{\cdot}320 \log c$, where c is the sodium concentration in milligram equivalents per litre. There is evidence to support the view that β refers to ionisation in two stages rather than to ionisation represented by $Na_2CO_3 = 2Na^{\cdot} + CO_3''$.

The experimental data lead to $k_3 = 4{\cdot}91 \times 10^{-11}$ for the second ionisation constant of carbonic acid at 25°, when the value for the first ionisation constant is taken as $k_2 = 3{\cdot}5 \times 10^{-7}$ (Kendall, A., 1916, ii, 512) and $k_w = 0{\cdot}82 \times 10^{-14}$. H. M. D.

Kinetic Theory of Reaction Velocity. A. MARCH (*Physikal. Zeitsch.*, 1917, **18**, 53—59).—A theoretical paper in which the author discusses the kinetics of the dissociation of a compound gas. It is assumed that dissociation occurs when the energy exceeds a certain critical value. If k is the velocity coefficient, then the influence of temperature on the velocity may be represented by the equation $d \log k/dT = A/T^2 + B/T + d \log dE/(dt/dT)$, in which dE represents the average value of the deviations of the energy during the interval of time dT from the mean energy content characteristic of the temperature T, and A and B are constants.

If dE/dt is constant, this formula becomes identical with that put forward by Kooy. The theory also leads to the conclusion that there is a certain critical temperature above which a chemical compound is incapable of existence. This temperature can be calculated from the heat of formation of the compound.

H. M. D.

The Landolt Reaction. J. EGGERT (*Zeitsch. Elektrochem.*, 1917, **23**, 8—19).—The author has evolved a theory to explain the time reaction occurring between iodates and sulphites in acid solution. This theory shows the connexion between the time of the reaction and the concentration of the reacting substances. In its chief points, the theory is confirmed experimentally; it is shown that the time of reaction is independent of the concentration of the sulphite ion, inversely proportional to the square of the iodate ion, and inversely proportional to the square of the concentration of the hydrogen ion. This last relationship only holds over a fixed range of concentrations. The time of the reaction is dependent only on two independent constants, k_1 and k_2, which are characteristic of the two main reactions, $3H_2SO_3+HIO_3=3H_2SO_4+HI$ (k_1), $5HI+HIO_3=3I_2+3H_2O$ (k_2), and can be experimentally determined. The time of reaction (T) can be calculated with satisfactory approximation by the formula $T=1/(k_2-k_1).\log_e k_2/k_1$. The inexactitudes of the theory are theoretically discussed. The influence of potassium iodide is to accelerate the reaction, and this can also be quantitatively calculated on the basis of the present theory. A number of experiments are described which show the influence of the concentration of the sulphite ion, iodate ion, and hydrogen ion on the rate of the reaction; a further series of experiments on the influence of the iodide ion is also described. The author regards the Landolt reaction as a case of autocatalysis.

J. F. S.

Fundamental Atomic Weights. ALOIS BILECKI (*Zeitsch. anorg. Chem.*, 1916, **98**, 86—96).—It has been shown by the author that many atomic weights are multiples of the number 0·31. Oxygen, however, does not fall into this arrangement, but it is now shown that if instead of the ratio $16:0·31=51·612$ the approximate ratio $16:52$ or $4:13$ be taken, new regularities are found. This ratio has the value $0·\dot{3}07692\dot{3}$, and may be called n. Taking the atomic weights of silver and bromine as $108=351n$ and $80=260n$ respectively, the deviations are well within the limits of the experimental error. Reducing this to the international value for silver, 107·88, bromine becomes 79·9111, n then becoming $n_1=0·30\dot{7}35042\dot{7}$. The following ratios are then obtained: $Ag=351n_1$, $Br=260n_1$, $Cl=115\frac{3}{8}n_1$, $I=413n_1$. Many elements with even valency are derived from n, and many with odd valency from n_1. The atomic weights of cobalt and nickel and of thorium and ionium differ by $1n$.

C. H. D.

The Latest Revisions of the International Table of Atomic Weights. PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 449—461).—A criticism of the annual reports issued by the International Committee on Atomic Weights. Apart from the fact that the changes recommended by the Committee do not appear to be warranted in many cases by the actual facts, it is claimed that the recommendations are not based on the application of any obvious general principles. The author puts forward a number of considerations which might with advantage be taken into account in the issue of future annual tables. When changes are recommended, the reasons should be clearly stated, and the relevant experimental data included in the report. Unless special circumstances require that the atomic weight of an element should be altered, it would be better for various reasons to revise the table every ten years instead of annually. H. M. D.

Isaac of Holland and Jan Isaac of Holland. W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 304—310).—An account of the work of two Dutch alchemists. A. J. W.

A Simple Apparatus for the Washing of Gases. HAROLD HEATH GRAY (T., 1917, **111**, 179—183).—The extraction of hydrocarbon or other vapours from mixtures in which the vapours are associated with permanent gases is usually effected by washing the gas by means of some liquid in which the vapour is readily soluble. The usual forms of "liquid" washers have the common drawback of interposing considerable resistance to the passage of the gas, but this difficulty is avoided by the use of a "vapour" washer, in which the gas to be washed is passed through a mass of condensing vapour of the solvent.

The washer described consists of a water-jacketed tube fitting tightly into the neck of a flask containing the heated solvent. The gas to be washed enters the flask through a narrower tube passing down inside the water-jacketed tube, which has an outlet for the washed gas at its upper end. The gas, heavily charged with vapour of the solvent, passes from the flask into the annular space between the inner tube and the water-cooled tube, where the vapour of the solvent is condensed and the substance to be estimated is thereby removed. The efficiency of the process is mainly due to the ideally intimate contact between the gas and the washing medium, but another important factor is that the solvent is continually present in large excess and in pure condition.

The apparatus has been employed for the extraction of toluene from coal-gas, in which case benzene may be employed as the "vapour" washing solvent. H. M. D.

A Removable, Universal Condenser. VIGREUX (*Bull. Soc. chim.*, 1917, [iv], **21**, 46—48).—A description of a simple form of reflux condenser which can be used with different flasks without the use of a cork for fitting it. Its efficacy is claimed to be high. W. G.

Inorganic Chemistry.

The Ignition Point of Detonating Gas. ALEXANDER MITSCHERLICH (*Zeitsch. anorg. Chem.*, 1916, **98**, 145—166).—Dry detonating gas, prepared electrolytically, is passed through a tube heated by means of a large, gas-heated copper tube, the temperature being measured by quartz–mercury thermometers reading up to 650°. When highly diluted with inert gas, no noise of explosion is perceptible, but the ignition point may be fixed by the appearance of a flash in a darkened room, even when the action is insufficient to cause any perceptible movement of the mercury in the manometer.

The ignition temperature is higher, the lower the velocity of the gas in passing through the tube, when the latter is low. At higher velocities, the temperature is independent of the velocity. The formation of water takes place below the ignition point, to an extent which varies with the condition and previous treatment of the glass tube. Silica tubes bring about a still greater formation of water below the ignition temperature, whilst very little is formed in tubes of glazed, and especially unglazed, porcelain which has been previously heated for a long time at 700°. C. H. D.

Electrolytic Formation of Perchlorate. C. W. BENNETT and E. L. MACK (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 323—346).—The formation of perchlorate at the anode is the result of direct oxidation by active oxygen. Sodium chlorate is largely oxidised to perchlorate by means of sodium persulphate, the yield being increased by the presence of a silver salt or by removing sulphate as formed by means of barium oxide. Ozone oxidises a small, but distinct, proportion of chlorate to perchlorate. Acid solutions of permanganates are without effect. Hydrogen peroxide forms hydrochloric, but not perchloric, acid. This action is probably due to the liberation of a little chlorine from the chloric acid, which then reacts with the hydrogen peroxide. Oxygen activated by ultra-violet light has the same effect as ozone. C. H. D.

General Considerations Relative to the Physico-chemical Revision of the Atomic Weight of Bromine on the Basis of the Normal Density of Gaseous Hydrogen Bromide. PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 361—388).—The chemical methods which have been employed in previous determinations of the atomic weight of bromine are subjected to a critical analysis in which it is shown that further observations are required before it is possible to assign to bromine an atomic weight value which is of the requisite order of accuracy. The advantages of the density method as applied to hydrogen bromide are indicated, and by way of introduction to a series of investigations in which the density of hydrogen bromide has been determined with the greatest possible

accuracy, the author gives an outline of improvements which have been effected in connexion with the experimental determination of gas densities and of the methods which may be most advantageously used in the reduction of the measurements of the density at pressures of 1, $\frac{2}{3}$, and $\frac{1}{3}$ atmosphere so as to obtain the ideal density which would be observed if the gas conformed absolutely to the requirements of the simple gas laws. H. M. D.

Revision of the Atomic Weight of Bromine. Determination of the Normal Density of Gaseous Hydrogen Bromide. ENRIQUE MOLES (*J. Chim. phys.*, 1916, **14**, 389—444).—The density of hydrogen bromide has been determined at 0° and at pressures of 1, $\frac{2}{3}$, and $\frac{1}{3}$ atmosphere, and from the data the molecular weight of hydrogen bromide and the atomic weight of bromine have been deduced.

The hydrogen bromide was prepared by four different methods: (1) hydrolysis of phosphorus tribromide, (2) action of bromine on hydrogen sulphide, (3) action of bromine on naphthalene, (4) action of bromine on paraffin. It was purified by chemical treatment and by liquefaction and fractional distillation, the efficacy of which process was increased by causing the gas to bubble through a portion of the liquefied substance between successive distillations.

Thirty-three determinations of the density at 0° and 760 mm. gave a mean value of 3·64442 grams for the weight of a litre of gas. The mean of eleven determinations at 506·67 mm. gave 2·42204 grams per litre, and the mean of seventeen determinations at 253·332 mm. gave 1·20737 grams per litre. When reduced to 760 mm. these became respectively 3·63314 and 3·62190 grams. From these numbers the coefficient of compressibility is calculated, and the value of λ in the expression $1+\lambda=(pv)_0/pv$ is thus found to be 0·00931. This number is employed in the calculation of the molecular weight of hydrogen bromide in terms of that of oxygen, for which $\lambda=0·00097$ and the weight of a litre at 760 mm. and 0° is taken as 1·42905. The molecular weight is thus given by $M=32\times 3·64442\times 1·00097/1·42905\times 1·00931=80·9333$. By taking H= 1·0076, this gives for the atomic weight of bromine Br=79·926.

This value is somewhat greater than that given by the chemical methods used at Harvard: Br=79·916 for Ag=107·880 or Br= 79·909 for Ag=107·871.

The ratio of the atomic weights of chlorine and bromine given by density measurements is 0·44367, which is identical with the value given by the Harvard determinations and by the measurements of Goldbaum and of Noyes and Weber. H. M. D.

The Revision of the Atomic Weight of Bromine. Density of Hydrogen Bromide Gas under Reduced Pressure. C. K. REIMAN (*Compt. rend.*, 1917, **164**, 180—181. Compare this vol., ii, 137).—Numerous determinations were made of the weight of a litre of hydrogen bromide at 506·67 mm. and 253·33 mm. From these results the values of a normal litre of the gas were calculated, the values for the two series being 3·6330 grams and 3·6218 grams

respectively. The variation from Avogadro's law between 0 and 1 atmos. is then calculated as being $1+\lambda=1{\cdot}00927$. From these results and those previously obtained (*loc. cit.*), the value for the atomic weight of bromine is deduced as 79·924, which is in close agreement with that obtained by Moles (A., 1916, ii, 314, 526; preceding abstract). W. G.

The Normal Density of Hydrogen Bromide Gas. W. J. MURRAY (*Compt. rend.*, 1917, **164**, 182—183).—The hydrogen bromide was prepared by the action of water on anhydrous aluminium bromide, carefully purified by fractional distillation. The mean of sixteen determinations gave the weight of a normal litre of hydrogen bromide as $3{\cdot}6440 \pm 0{\cdot}0005$ grams, which is in close agreement with the values obtained by Moles (A., 1916, ii, 314, 526) and Reiman (this vol., ii, 137; preceding abstract). W. G.

A New Method of Determining the Atomic Weight of Iodine. MARCEL GUICHARD (*Ann. Chim.*, 1916, [ix], **6**, 279—318; 1917, [ix], **7**, 5—49).—A full account of work already published (compare A., 1914, ii, 723). W. G.

The Action of Ozone on Inorganic Iodine Compounds. E. H. RIESENFELD and F. BENCKER (*Zeitsch. anorg. Chem.*, 1916, **98**, 167—201).—Harries (A., 1912, i, 407) has assumed the presence of a new modification of oxygen, O_4, in ozone. The oxidising power of ozone towards iodine compounds has hitherto been examined only in acid, neutral, and alkaline solutions of potassium iodide. The reactions with iodine, iodates, and periodates have not been investigated. Ozone reacts with solutions of potassium iodide instantaneously, even below 0°, but the final equilibrium in the solution between $K^{\cdot}$, OH', I', IO', IO_3', and IO_4' is only attained after some days. The higher the concentration of the ozone in the oxygen used, the greater is the influence of the hydroxyl ions. In acid solutions the ordinary reaction is accompanied by one in which 3 atoms of oxygen from a molecule of ozone take part, the 'oxidation number' being independent of the ozone concentration, but increasing with the acid concentration and with falling temperature, the highest value actually obtained being 2·7. The higher reaction may be an addition of ozone to iodine ions, forming iodate, or a formation of hydrogen peroxide. In either case the product at once reacts with the excess of iodide, and free iodine is the final product. The value 1 is not much altered by the addition of salts.

Ozone is without action on neutral and acid solutions of potassium iodate, but in alkaline solution oxidation to periodate takes place. Ozone is without action on periodate. There is no evidence for the existence of a modification of oxygen containing more than three atoms, the differences observed by Harries between the results of gravimetric and volumetric estimations being due to the action of hydroxyl ions. C. H. D.

The Preparation of Fluorine from Hydrogen Fluoride or other Fluorides by Chemical Means. OTTO RUFF (*Zeitsch. anorg. Chem.*, 1916, **98**, 27—37).—The only chemical method for the

preparation of fluorine is that of Brauner (T., 1894, **65**, 393) by heating the double salt, $3KF,HF,PbF_4$ (compare following abstract). This result has not been confirmed, the products of decomposition by heat being lead difluoride and platinum tetrafluoride when a platinum vessel is used. Liquid or gaseous silicon tetrafluoride is practically without action on the double salt, a small quantity of gas acting on potassium iodide–starch paper being obtained at 250°, but without altering the composition of the salt. A larger quantity is obtained by the use of antimony pentafluoride. Sulphur and iodine form sulphur fluoride and iodine pentafluoride respectively.

[With WILHELM PLATO.]—*Triammonium hydrogen plumbofluoride,* $3NH_4F,HF,PbF_4$, is prepared by dissolving lead tetraacetate in concentrated hydrofluoric acid and adding ammonium hydrogen fluoride, filtering, and evaporating. The salt may be heated at 190° under atmospheric pressure or even under 10 mm. pressure without change, but in a good vacuum decomposition takes place at 100°, nitrogen being evolved.

[With GEORG WINTERFELD.]—It has not been found possible to prepare lead tetrafluoride by the action of sulphuric acid on Brauner's double salt, or by the action of hydrofluoric acid under various conditions on lead tetra-acetate. C. H. D.

The Preparation of Fluorine from Tripotassium Hydrogen Plumbofluoride by Chemical Means. BOHUSLAV BRAUNER (*Zeitsch. anorg. Chem.*, 1916, **98**, 38—46. Compare preceding abstract).—The differences between the results obtained by the author in 1894 and those of Ruff are not explained. The earlier lead preparation contained manganese, which may have acted as a catalyst, or the gas evolved by heating may not have been fluorine. It is, however, shown that silicon does not inflame spontaneously in dry hydrogen fluoride. C. H. D.

New Determination of the Atomic Weight of Tellurium. ARTHUR STÄHLER and BRUNO TESCH (*Zeitsch. anorg. Chem.*, 1916, **98**, 1—26).—Tellurium is best purified by fractional distillation, which removes nearly all impurities except antimony. Conversion into chloride and distillation of the product removes many impurities, including antimony. For the investigation, tellurium is first distilled twice in a vacuum, converted into the tetrachloride, and fractionally distilled in a stream of chlorine, the latter operation being repeated five times. The tetrachloride is dissolved in concentrated hydrochloric acid, diluted, and precipitated by sulphur dioxide, the precipitating vessel being enclosed in an autoclave under 18—20 atmospheres pressure to ensure complete reaction. The amorphous product is dried, fused, and fractionally distilled in a good vacuum, electrolytic hydrogen being used to fill the apparatus. The temperature being near to the softening point of Jena glass, the final distillation is performed in a silica tube. The tellurium obtained in this way, from three different sources, in all cases proves to be spectroscopically free from impurities.

Tellurium is converted into the dioxide by dissolving in nitric

acid and heating in a stream of dry air, the basic nitrate then being decomposed by heat. The nitric acid which distils over is collected and evaporated, and yields a further small quantity of tellurium dioxide. The value obtained for the atomic weight (O=16) is 127·513 ± 0·003. C. H. D.

Tellurium Perchlorate. FR. FICHTER and MAX SCHMID (*Zeitsch. anorg. Chem.*, 1916, **98**, 141—144).—Iodine perchlorate having been previously obtained (A., 1915, ii, 253), the attempt has now been made to prepare tellurium perchlorate. Tellurium dioxide dissolves readily in warm concentrated perchloric acid to a clear solution, which deposits glistening, hexagonal leaflets on cooling. These are drained, washed with anhydrous alcohol out of contact with air, and dried in a stream of dry air. For analysis, the salt is decomposed by means of warm sodium acetate solution, the tellurium dioxide collected in an alundum crucible and dried, and perchlorate estimated in the filtrate by precipitation with nitron. The analysis is also controlled by reduction to tellurium by means of hydrazine hydrate.

Tellurium perchlorate has the composition $2TeO_2,HClO_4$, corresponding with the known basic nitrate, $2TeO_2,HNO_3$. It may be heated to constant weight at 300° without decomposition.
C. H. D.

Phospham. F. W. DAFERT and ALFRED UHL (*Zeitsch. landw. Versuchs-Wesen, Osterr.*, 1916, **19**, 389—392; from *Chem. Zentr.*, 1917, i, 162).—The authors have endeavoured to determine whether oxides of nitrogen are actually formed during the oxidation of phospham, and, if so, to what extent the formation occurs. The crude material, prepared according to the directions of Liebig and Wöhler, was used, since the complete purification of phospham has not yet been effected. For the experiments, weighed portions of the finely-powdered material were mixed in a porcelain boat with the requisite oxidising agent and heated in a glass or porcelain tube. The escaping gases were bubbled through standard potassium hydroxide solution. Of the oxidising agents employed (BaO_2, $PbCrO_4$, PbO_2, MnO_2, $KMnO_4$, CuO, etc.), silver oxide was found to give the most uniform results and also to act at a comparatively low temperature. In these circumstances, exactly one-half of the nitrogen contained in phospham is eliminated in the form of nitrogen compounds, whilst the other half is evolved in the elementary condition. This is probably accounted for by the difference in the mode of linking of the nitrogen atoms in the phospham molecule, N:P:NH. Phospham is not greatly changed in the soil, and cannot serve as a source of nitrogen or phosphorus for plants. H. W.

Compounds of Arsenious Oxide and Salts. III. F. A. H. SCHREINEMAKERS and (MEJ) W. C. DE BAAT (*Chem. Weekblad*, 1917, **14**, 244—248. Compare this vol., ii, 173).—An investigation of the behaviour of arsenious oxide with haloids of the alkali and alkaline-earth metals. The chlorides of lithium, sodium, calcium, and stron-

tium, and the bromides of calcium and strontium, do not form compounds. The chlorides of potassium, ammonium, and barium, the bromides of lithium, sodium, potassium, ammonium, and barium, and potassium iodide yield derivatives of varying composition. A. J. W.

Boric Anhydride and its Hydrates. JAMES ECKERSLEY MYERS (T., 1917, **111**, 172—179).—The relations between boric anhydride, metaboric acid, and orthoboric acid have been examined.

When a potassium iodide–iodate solution is added to a solution of orthoboric acid, iodine is liberated after one or two minutes. When solutions of boric anhydride and metaboric acid are similarly treated, iodine is liberated much more slowly, and in some cases it was found that two or three hours were required to produce the same effect as that obtained with orthoboric acid. Some specimens of metaboric acid react more quickly than others, and it is suggested that this may be due to a difference in the molecular complexity.

Further information relative to the hydration of boric anhydride was obtained by observations on the rate of increase in weight of the substance when exposed in a thin layer to an atmosphere saturated with water-vapour at a constant temperature. The results obtained show that the hydration takes place in two stages, the formation of metaboric acid in the first stage taking place much more quickly than that of orthoboric acid in the second. Other experiments by the same method with metaboric acid show that the progress of the hydration may be satisfactorily represented by the equation for a unimolecular change.

A study of the dehydration of orthoboric acid at about 100° has afforded evidence that metaboric acid is produced at a rate consistent with the equation for a unimolecular change. At higher temperatures the dehydration seems to result in the formation of molecular complexes of metaboric acid. H. M. D.

Nomenclature of Silicon Compounds. ALFRED STOCK (*Ber.*, 1917, **50**, 169—170. Compare A., 1916, ii, 319).—Perhaps the greatest confusion in the nomenclature of silicon compounds is to be found in the case of substances containing the –Si–O–Si– system. It is proposed to call the parent hydrogen compounds of this type "siloxanes," and to specify the number of silicon and oxygen atoms in such terms as "disiloxane," "disildioxane," etc. For example, $(SiCl_3)_2O$ would be the formula of "hexachlorodisiloxane," and the compound,

$$\underbrace{SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2}_{O}$$

would be "octaphenyltetrasiltetroxane." It is not proposed to modify the accepted terminology in the case of polysilicates and polysilicic acids. J. C. W.

Silicon Chemistry and Carbon Chemistry. ALFRED STOCK (*Ber.*, 1917, **50**, 171—182).—From the fact that about five hundred compounds of silicon are now known, exclusive of the silicic acids

and silicates, the question can be discussed whether the earlier chemists were justified in believing that it only required time and opportunity to develop a silicon chemistry analogous to that of carbon, or whether Moissan was right in denying such a close analogy. The material is now reviewed in an interesting manner under the headings of the following linkings: Si–H, Si–C, Si–Hal., Si–N, Si–Si, Si=Si, Si–O, and Si–O–Si, and the well-known differences between carbon and silicon in such combinations are emphasised.

Perhaps the chief reason why it has been possible to extend carbon chemistry so enormously is the fact that the affinity of carbon is about equally strong for positive and negative non-metallic elements. (for example, H, O, S, N, Cl, or C). Although the maximum valency of silicon is also four with regard to both hydrogen and oxygen, yet there is an enormous difference between the positive and negative affinities. The affinity for oxygen is so predominant that practically all other silicon linkings are broken down by the action of cold water.

A further difference between carbon and silicon which would account for many of the divergences in the two series is that the four valencies are symmetrically distributed in carbon, but not in silicon (compare Barlow and Pope, T., 1908, **93**, 1554). J. C. W.

The Reactivity of Silica with the Oxides of Calcium, Barium, and Magnesium in the Solid State. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **98**, 57—69).—The reactions between these oxides have been investigated by means of heating and cooling curves. Lime and precipitated silica react at 1011°, but the reaction comes to a standstill owing to the formation of a layer of metasilicate. A more vigorous reaction begins shortly above 1400°, owing to the eutectic temperature of the lime–silica system being reached. The reactivity of other varieties of silica diminishes in the order: silica glass, cristobalite, quartz. Calcium carbonate is acted on to a small extent by precipitated silica at or below 900°, possibly owing to the presence of a larger proportion of small particles, but the lime formed at the dissociation temperature is not specially reactive. Precipitated silica reacts with barium oxide at 900°, whilst no arrest has been observed on the heating curve of a mixture of silica and magnesia. C. H. D.

Carbon Oxysulphide, COS. ALFRED STOCK and ERNST KUSS (*Ber.*, 1917, **50**, 159—164).—Carbon oxysulphide may be obtained by the action of hydrochloric acid on commercial ammonium thiocarbamate, according to the equation $NH_4 \cdot CO \cdot S \cdot NH_2 + 2HCl = COS + 2NH_4Cl$. In order to purify it, it is bubbled through 33% sodium hydroxide to absorb carbon dioxide and hydrogen sulphide, dried by means of calcium chloride and phosphoric oxide, then condensed by means of liquid air, and finally fractionated.

The pure gas is odourless and does not at once give a precipitate with barium hydroxide or copper sulphate solution. It is slowly decomposed by water, but in the dry state it is permanent even in sunlight.

It has $D^{-87^{\circ}}$ 1·24, m. p. −138·2° (CO_2, −56·4°, CS_2, =112·1°), b. p. −50·2°/760 mm. (CO_2, −78°; CS_2, 46°). One part of water dissolves 0·54 vol. at 20°, 1 part of alcohol dissolves 8 vols. at 22°, and 1 part of toluene 15 vols. at 22°.

It is slowly and regularly absorbed by 33% sodium hydroxide (about 2% per minute), much more readily by an 8% solution (33% per minute), or by a 23% solution of potassium hydroxide (8% per minute). It is therefore quite possible to estimate readily absorbable gases in the carbon oxysulphide by using 33% sodium hydroxide, and allowing for the loss of the latter gas during the time of the absorption. J. C. W.

Sodium Arsenites. F. A. H. SCHREINEMAKERS and (MEJ) W. C. DE BAAT (*Chem. Weekblad,* 1917, **14**, 262—267, 288—290).—An application of Schreinemakers's graphic method to the equilibria in the system water–arsenious oxide–sodium hydroxide at 25°. A. J. W.

Water Content of Crystalline Sodium Tetraborate. J. HOFFMANN (*Chem. Ind.*, 1916, **39**, 411—412; from *Chem. Zentr.*, 1917, i, 304).—Estimation of the loss of water of crystallisation of sodium tetraborate at different temperatures has shown that the first five molecules begin to be lost below 100°, whilst six molecules are lost at 100°; the seventh and eighth molecules escape at 130°, the ninth at 150°, whilst the tenth is evolved at 160° and above. At the ordinary temperature crystalline borax has the formula $Na_2B_4O_7,10H_2O$; at 100°, $Na_2B_4O_7,5H_2O$; at 130°, $Na_2B_4O_7,3H_2O$; at 150°, $Na_2B_4O_7,2H_2O$; at 180°, $Na_2B_4O_7,H_2O$. The penultimate molecule of water of crystallisation is retained more firmly than the others, and prolonged heating is necessary to remove it. Borax of the composition, $Na_2B_4O_7,H_2O$, exists in traces far above this temperature, but below 318° the bulk of the water is driven off. When it is desired to obtain practically anhydrous borax in the non-glassy form, the crystalline material is heated at 318° (m. p. of potassium nitrate). Absolutely anhydrous borax is difficult to obtain in the non-glassy state, since the dehydrated powder absorbs water more readily than the glassy material. The latter during five months only absorbs 0·4% of water, whilst this amount is absorbed by the former in twenty-four hours. After sixteen months the powdered form had absorbed 10, the glassy 0·6, molecules of water. H. W.

The Internal Field of the Lithium Atom. A. HARTMANN (*Physikal. Zeitsch.*, 1917, **18**, 14—16).—According to Watts, the line series of the alkali metals are most satisfactorily represented by the Mogendorff–Hicks formula. By neglecting the smaller coefficients this passes into the Balmer formula, and from this it would seem that the structure of the lithium atom is similar to that of the hydrogen atom. If this be the case, two of the three electrons are probably in close proximity to the positive nucleus, and take no part in the emission of the characteristic radiation.

By assuming that the internal electric field is symmetrical and

by making use of Bohr's theory relative to the nature of the emission phenomenon, the author has calculated the magnitude of the force due to the action of the nucleus on the rotating electrons when the number of these is one, two, and three respectively. From the result the apparent charge of the nucleus is derived, and for the three cases referred to it is found that the charge is represented by e, $5/4e$, and $(1+1/\sqrt{3})e$ respectively. The result of the calculation is considered to be favourable to the view that the lithium atom contains a single active electron, the two others being in relatively close proximity to the positive nucleus and neutralising thereby two-thirds of the positive charge. H. M. D.

Allotropy of the Ammonium Haloids. III. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 798—804. Compare A., 1916, ii, 31, 431).—Further observations on the relation between the α- and β-forms of ammonium bromide show that the transformation is facilitated by the addition of glycerol, and in presence of this, the transition point, as determined by the thermal method, was found to lie between 137·3° and 139·5°. Measurements of the solubility of ammonium bromide in water at temperatures between 95° and 158° show evidence of two solubility curves intersecting at 137·4°, which agrees well with the value recently recorded by Smith and Eastlack (A., 1916, ii, 482). If x is the molar fraction of ammonium bromide in the saturated solution, the solubility below the transition temperature is given by $\log x = -372{\cdot}7/T + 0{\cdot}31978$, and above the transition temperature by $\log x = -293{\cdot}7/T + 0{\cdot}12727$. Measurements of the vapour pressures of the saturated solutions gave no evidence of a break at 137°, the vapour pressure at temperatures between 98° and 157° being satisfactorily represented by the equation $\log p = -1927{\cdot}6/T + 6{\cdot}8302$.

By means of thermal observations it has been found that ammonium iodide also exists in two forms, and that the transition point lies between −17·2° and −15·6°. The transformation appears to be accelerated by the addition of small quantities of water. It has been found possible to observe that transition point and the eutectic point for the system NH_4I-H_2O at −28° in the same cooling experiment. According to the observations of Smith and Eastlack (A., 1916, ii, 529), extending from −19° to 136°, there was no evidence of the existence of two modifications of ammonium iodide. H. M. D.

Synthesis of a Basic Calcium Salt, on the Ground of a Change of Properties of Milk of Lime. N. Busvold (*Zeitsch. anorg. Chem.*, 1916, **98**, 202).—The power of milk of lime to resist settling is increased by the addition of calcium nitrate, a maximum value for the permanence being found at the composition $2CaO,Ca(NO_3)_2$. By slaking quicklime with a concentrated solution of calcium nitrate, white needles of the salt

$$2Ca(OH)_2,Ca(NO_3)_2,2H_2O,$$

are obtained, which become turbid on the addition of water.

C. H. D.

The Temperatures of Formation and Decomposition of the Carbonates of Calcium, Strontium, Barium, and Magnesium under a Pressure of One Atmosphere. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **98**, 47—56).—Dissociation temperatures may be determined more rapidly by taking heating and cooling curves than by measurements of pressure. Calcium carbonate gives a well-marked arrest on heating, but the contraction on formation of lime makes the mass so little reactive that the cooling curve is continuous. On increasing the surface of the lime by grinding, however, the absorption of carbon dioxide is hastened, and a corresponding arrest is found on the cooling curve. The dissociation temperature of calcium carbonate is thus found to be 913—923°, this being independent of the size of grain. The dissociation of strontium carbonate begins at 1141°, but only becomes rapid at 1255°. Barium carbonate only begins to dissociate at 1361°, its melting point. Magnesium carbonate dissociates at 546°. C. H. D.

Cadmium and Zinc Nitrites. PRAFULLA CHANDRA RÂY (T., 1917, **111**, 159—162).—Cadmium nitrite, prepared by trituration of cadmium chloride with silver nitrite, extraction with water, and evaporation in a vacuum, forms bright, pale yellow crystals of the composition $Cd(NO_2)_2$. According to conductivity measurements, the nitrite is appreciably less ionised than the chloride in 0·1*N*-solution. On the other hand, its ionisation is much greater than that of mercuric nitrite. The greater tendency of cadmium, as compared with mercuric nitrite, to form basic salts may be explained in terms of this difference in the ionisation of the two salts.

On heating, cadmium nitrite begins to decompose at about 150°. The main reaction compares with $3Cd(NO_2)_2 = 2CdO + Cd(NO_3)_2 + 4NO$, but some nitrite also decomposes amounting to $Cd(NO_2)_2 = CdO + NO + NO_2$.

The solution obtained by the interaction of zinc sulphate and barium nitrite evolves nitric oxide when concentrated by evaporation, and the residue consists of a basic zinc nitrate. H. M. D.

The Solubility of Lead Sulphate in Highly Concentrated and Fuming Sulphuric Acid. HUGO DITZ and FRANZ KANHÄUSER (*Zeitsch. anorg. Chem.*, 1916, **98**, 128—140).—The solubility of lead sulphate in highly concentrated sulphuric acid, as in the manufacture of acid by the contact process, is greater than appears in the literature. Acid of various concentrations is added to dry lead sulphate in stoppered bottles, and shaken from time to time, the solubility being determined after three days. The solution is filtered through asbestos by means of suction. The solubility increases with the concentration of the sulphuric acid, slowly up to 97%, then rapidly up to 100%, a discontinuity observed between 98·6% and 98·9% being possibly due to experimental error. From the maximum solubility at 100%, the curve falls to about 5% of free

sulphur trioxide, where there is a minimum, after which it again rises rapidly to 15% of trioxide, and then less rapidly to 22%.

The known curve of electrical conductivity of sulphuric acid is very similar to the curve just described. The degree of attack of highly concentrated sulphuric acid on metallic lead also corresponds in general with the same curve. C. H. D.

Neodymium as the Cause of the Red-violet Colour in certain Minerals. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1917, **7**, 143—146).—The author shows that the reddish-violet colour of many minerals cannot be due to the presence of permanganates, as has been often assumed. The reasons advanced against the generally accepted view are: (1) permanganates can only be formed by vigorous reactions which would in many cases destroy the mineral; (2) many minerals showing a violet-red colour also contain ferrous iron, and consequently may be assumed to have been formed under reducing conditions; and (3) these minerals do not exhibit the characteristic absorption spectrum of the permanganates. A careful examination of reddish-violet-coloured minerals by means of a microspectroscope shows that these minerals all exhibit the absorption spectrum of neodymium compounds. This spectrum has been very clearly observed in brown apatite from Ontario, violet apatite from California, and in reddish-violet calcites. J. F. S.

The Passive State of Metals. C. W. BENNETT and W. S. BURNHAM (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 217—254).—The passive state of metals may be regarded as one in which solution takes place slowly. Faraday's oxide or oxygen theory was generally accepted until it was shown by Hittorf that passive chromium dissolved quantitatively in most solutions as a sexavalent ion. The evidence for and against the oxide explanation is now reviewed, with a full bibliography. The oxide may be regarded as forming a film which is rendered stable by adsorption into the metal. The oxide is usually unstable, and only becomes stable on adsorption. In the case of chromium, the oxide is not higher than CrO_3, and is probably $CrCrO_4$, or CrO_2, but in the further oxidation at the anode the higher oxide is formed, and chromium dissolves in the sexavalent state. The oxide of iron is not higher than FeO_3, and may be FeO_2.

A case of an unstable substance being rendered stable by adsorption is that of cupric hydroxide, which is not decomposed to oxide on boiling with water in presence of manganese sulphate, which is adsorbed by the precipitate, or when itself adsorbed by wool. Iron is made passive by dipping in a solution of potassium ferrate, and chromium by potassium chromate. Lead usually becomes passive by the formation of lead peroxide, but in concentrated sulphuric acid at a low temperature lead dissolves as a quadrivalent ion.

All the phenomena of passivity are explainable on this hypothesis. C. H. D.

The Corrosion and Electrical Properties of Steels. SIR ROBERT HADFIELD and EDGAR NEWBERY (*Proc. Roy. Soc.*, 1917, *A*, **93**, 56—67).—The steels, having uniformly rubbed surfaces prepared by means of emery, are coated with wax so as to expose a constant area, and after immersing in *N*-sulphuric acid, the overvoltage is determined (T., 1914, **105**, 2420). The electrodes are then washed, dried, again rubbed with emery, and their potential in *N*-sulphuric acid measured against a mercurous sulphate electrode. The sum of this single potential and the overvoltage at the lowest current density used is regarded as a measure of the resistance to corrosion. This is compared with the loss in weight when the same steel is exposed to the same acid solution, and with the tendency to rusting on exposure to the atmosphere of the laboratory. The electrical measurements correspond much more nearly with the atmospheric corrosion than do the losses on immersion in acid. No great accuracy is yet possible, and in certain cases, such as steel with more than 12% of chromum, which is quite unaffected by exposure to the atmosphere, both the electrical and the acid methods greatly underestimate the resistance to corrosion.

C. H. D.

Chromium Phosphate. ALFRED FRANCIS JOSEPH and WILLIAM NORMAN RAE (T., 1917, **111**, 196—202).—When equal weights of chrome alum and disodium hydrogen phosphate are mixed in cold solution, an amorphous precipitate of violet chromium phosphate is obtained. When allowed to remain in contact with the solution for a day or two, this is transformed into a crystalline modification of the composition $CrPO_4,6H_2O$. If the contact is prolonged for a week, the crystalline hexahydrate is converted into a green, amorphous tetrahydrate. This change also occurs in contact with pure water, but is accelerated by sodium phosphate or chrome alum, and is also influenced largely by the temperature. If the violet hexahydrate is heated or boiled with water, it is transformed into a green, crystalline tetrahydrate. If boiled with acetic anhydride, the hexahydrate forms a green, crystalline dihydrate. The crystalline di- and tetra-hydrates when heated to low redness are converted into black, anhydrous chromium phosphate. The densities of the crystalline hydrates were measured, and attempts made to determine the rate of dehydration.

Precipitation of a hot chrome alum solution with excess of disodium hydrogen phosphate gave a green, amorphous chromium phosphate, which rapidly lost water at the ordinary temperature until the composition $CrPO_4,4H_2O$ was attained. At 60° a further loss of 2 molecules of water took place, and on heating to dull redness a brown, amorphous chromium phosphate was obtained.

The behaviour of the hydrated and anhydrous forms towards mineral acids is described in detail, and reference is made to an abnormally great loss in the weight of platinum crucibles when heated in a gas furnace at 1100°, although no loss was found when heating took place in an electric furnace at the same temperature but with practically no air current. H. M. D.

The Constitution of the Tin-Cadmium and Tin-Bismuth Alloys. ARMIN BUCHER (*Zeitsch. anorg. Chem.*, 1916, **98**, 97—127).—The alloys, after melting in a vacuum, are forced up into an evacuated tube sealed at the top, by admitting air into the outer vessel. By breaking away the glass, smooth rods are obtained. The electrical conductivity and its temperature-coefficient, and the thermo-electromotive force, are then determined, pure silver being used as the comparison metal. Tin and cadmium are reciprocally soluble to the extent of 3% in the solid state, the conductivity and thermo-electric curves being straight between those limits. The solubility of tin in solid cadmium falls with falling temperature. Microscopical examination confirms the above results.

Tin holds up to 14% of bismuth, and bismuth holds up to 1·5% of tin, in solid solution. The conductivity curve is of the expected form, but the temperature-coefficient curve and the curve of thermo-electromotive force exhibit strongly marked discontinuities at the eutectic composition. This appears to be connected with the microscopic structure, alloys on the tin side of the eutectic point being fine-grained, whilst those containing free bismuth are very coarse. C. H. D.

Equilibria between Titanium Dioxide and Carbon Dioxide, and between Silica and Carbon Dioxide, in Alkali, Lime-Alkali and Alkali-Aluminate Fusions. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1916, **98**, 241—326. Compare A., 1913, ii, 1036).—For the investigation of the system K_2O–TiO_2–CO_2, pure titanium dioxide is added to potassium carbonate in a platinum crucible in a continuous stream of carbon dioxide. After equilibrium has been reached, the crucible is quenched and allowed to cool in a desiccator which does not contain carbon dioxide. Under similar conditions, less carbon dioxide is expelled by titanium dioxide than by silica. The solid phase formed is $K_2Ti_2O_5$, the reaction beginning in the solid state, but only becoming rapid at about 860°. Carbon dioxide is absorbed on cooling, so that equilibrium may be reached from both directions. Treatment with hydrochloric acid leaves only titanium dioxide, in the form of transparent pseudomorphs after the titanate. In the molten mass other titanates, probably K_2TiO_3, are formed.

In the system Na_2O–TiO_2–CO_2, the solid titanate readily separates from the fusion, and there is also loss of sodium carbonate by volatilisation. Carbon dioxide is also frequently evolved during solidification. The principal solid phase is $4Na_2O,5TiO_2=Na_8Ti_5O_{14}$, but a titanate, $Na_2Ti_3O_7$, is also formed, as well as Na_2TiO_3 at high temperatures. $Na_8Ti_5O_{14}$ crystallises in forms resembling augite. The refractive index is more than 1·74.

The silicates and titanates obtainable from fusions are comparable with hydrated salts, silica and titanium dioxide playing a part similar to water of crystallisation.

In the system Na_2CO_3–$CaCO_3$, the double salt, $Na_2CO_3,CaCO_3$, forms large crystals, m. p. 813°. Mixtures containing more than 50 mol. % of calcium carbonate deposit calcite as the second solid

phase. The eutectic point between the double salt and the solid solution rich in sodium carbonate is at 786° and 40 mol. % $CaCO_3$, the solid solution curve passing through a maximum at about 870°. The eutectic point in the system K_2CO_3–$CaCO_3$ is at 755° and 40 mol. % $CaCO_3$, the solid solution curve being without a maximum. The compound $K_2CO_3,CaCO_3$ melts at 813°, and closely resembles the sodium compound.

In the system K_2O–CaO–TiO_2–CO_2, fusions containing an excess of calcium carbonate convert the whole of the added titanium dioxide into perowskite, $CaTiO_3$. Any excess of titanium above this proportion forms $K_2Ti_2O_5$. The facts are in accordance with the frequent occurrence of perowskite as a product of the contact metamorphosis of limestone. The corresponding sodium system is quite similar. The product when silica is added to potassium and calcium carbonates is the orthosilicate, Ca_2SiO_4, and when wollastonite, $CaSiO_3$, is added to the carbonate fusion it is converted into the orthosilicate. Ca_2SiO_4 and $CaCO_3$ may occur together as solid phases from the same fusion at about 850° under atmospheric pressure in carbon dioxide. When alumina is present, silica first acts on the carbonate as if alumina were absent, but the silicate then reacts with alumina, so that an alkali aluminosilicate crystallises, and the liberated alkali then recombines with carbon dioxide. With potassium carbonate, potash–nepheline, $K_2O,Al_2O_3,2SiO_2$, is the product from all fusions. Orthoclase is decomposed by alkali carbonate, forming potash–nepheline, the silica thus liberated forming alkali silicate. A ternary diagram for the system K_2O–Al_2O_3–SiO_2 is given. C. H. D.

Iso- and Hetero-polyacids. XIV. Heteropolyvanadates. ARTHUR ROSENHEIM and MARIANNE PIECK (*Zeitsch. anorg. Chem.*, 1916, **98**, 223—240. Compare this vol., ii, 35).—The ammonium salt obtained from diammonium hydrogen phosphate and vanadium pentoxide (Friedheim, A., 1890, 1067; 1894, ii, 193, 198) has the constitution $(NH_4)_7[P(V_2O_6)_6],13H_2O$, but loses ammonia on recrystallisation, forming $5(NH_4)_2O,P_2O_5,12V_2O_5,44H_2O$. The potassium salt is still more hydrolysed, the only product isolated having the composition $5K_2O,P_2O_5,10V_2O_5,50H_2O$, the conductivity of which indicates that it is $K_5H_2\left[P\begin{matrix}(V_2O_6)_5\\ O\end{matrix}\right],24H_2O$. The heptabasic ammonium salt forms a crystalline precipitate with cæsium chloride, having the composition $5Cs_2O,P_2O_5,10V_2O_5,27H_2O$. This and the corresponding rubidium salt (with $46H_2O$) contain 2 mols. of combined water.

The salts containing vanadium and tungsten all contain combined water. Thus, $2BaO,V_2O_5,4WO_3,13H_2O$ contains $1H_2O$ in combination; $2Ag_2O,V_2O_5,4WO_3,2H_2O$ contains 2 mols., and the guanidinium salt, $2(CH_6N_3)_2O,V_2O_5,4WO_3,H_2O$, 1 mol. This is also the case with the salts having the colour of dichromates. In the purple series, the ammonium salt is now found to be

$$5(NH_4)_2O,3V_2O_5,14WO_3,37H_2O,$$

containing 5 mols. of combined water. The guanidinium salt, $5(CH_6N_3)_2O,3V_2O_5,14WO_3,12H_2O$, contains 5 mols. of combined

water. The cæsium salt contains 2 mols. of water of crystallisation and 5 mols. of combined water. C. H. D.

Volatility of Gold at High Temperatures in Atmospheres of Air and other Gases. W. MOSTOWITSCH and W. PLETNEFF (*J. Russ. Metall. Soc.*, 1915, 410—431; *Met. and Chem. Eng.*, 1917, **16**, 153—154; from *J. Soc. Chem. Ind.*, 1917, **36**, 341). Fused samples of purified gold (0·2—0·5 gram) were placed in an unglazed porcelain or quartz boat and submitted to a stream of gas for measured intervals, extending up to two and a-half hours, while heated in a Heraeus furnace at temperatures between 1100° and 1400°. The metal was weighed before and after each experiment by means of a micro-balance. In atmospheres of oxygen, nitrogen, carbon monoxide, or carbon dioxide, no loss of weight could be detected at temperatures up to 1400°. With hydrogen, however, volatilisation was observed, amounting at 1400° after an interval of twenty-five minutes to 0·98 mg., corresponding with a loss of 0·25%. The vaporisation was accompanied by a deep red colouring of the silica boat and the heating tube, due to the formation of a colloidal solution of gold in the quartz. This action is analogous to similar phenomena shown by copper when heated in hydrogen, and leads to the supposition that, at temperatures above 1200°, an unstable hydride, such as Au_2H_2, is successively formed and decomposed. H. W.

Mineralogical Chemistry.

The Rôle of Inorganic Agencies in the Deposition of Calcium Carbonate. JOHN JOHNSTON and E. D. WILLIAMSON (*J. Geology*, 1916, **24**, 729—750).—The authors discuss the effects producible by variation of certain factors which affect directly the solubility of calcium carbonate, and thus induce its precipitation from aqueous solution. The factors concerned are the partial pressure of the carbon dioxide in the atmosphere, the temperature, and the concentration of the solution in respect of calcium. At a given temperature, the equilibrium between calcite and its saturated solutions is determined by the coefficient of solubility of carbon dioxide, the ionic solubility product, $[Ca^{\cdot\cdot}][CO_3'']$, the ionisation-coefficients of carbonic acid, and the coefficient of hydrolysis of calcium carbonate. The free and the total carbonic acid, that is to say, $[H_2CO_3] + [CO_3''] + [HCO_3']$, determine the degree of alkalinity or acidity of the solution as measured by $[OH']$, and no change can be made in any one of these quantities without affecting each of the others. At 16°, the solubility of calcite increases from 44 to 75 parts per million, when the partial pressure of the carbon dioxide increases from 0·0001 to 0·0005. Under atmospheric conditions for which the mean value of the partial pressure may be taken as 0·00032, the

solubility decreases from 81 parts per million at 0° to 52 parts at 30°. A change in the partial pressure from 0·00032 to 0·00030, or an increase of temperature of 2°, would result ultimately in the precipitation of about 2 grams of calcite from every cubic metre of a solution saturated with it.

Comparison of the calculated solubilities with the available analytical data indicates that the warmer surface layers of the sea are substantially saturated with respect to calcite, and precipitation is consequently to be anticipated if there is a reduction in the partial pressure of the atmospheric carbon dioxide or a rise in temperature of the surface layers in question.

In regard to biological processes which result in the deposition of calcite, it is pointed out that the above-mentioned inorganic factors must be taken into account, no matter what may be the agency which is supposed to be directly responsible for the deposition. There are grounds for believing that calcareous organisms are more abundant the more nearly saturated the water is in respect of calcium carbonate, and it is suggested that the decreasing abundance of calcareous organisms toward the polar regions is a question, not only of the decrease of general vitality but also of the decreasing capacity of the organism to secrete calcium carbonate from colder sea-water in which the degree of unsaturation is greater than for the same water at a higher temperature.

Although arragonite is occasionally formed in nature, it is considered that pure arragonite cannot persist in contact with sea-water for any length of time. If, however, the arragonite takes up other substances in the form of a solid solution, and its solubility is thereby reduced below that of calcite, it is possible that such impure arragonite may be stable in contact with sea-water.

It is considered that the accurate determination of temperature, salinity, and free and combined carbonic acid in sea-water in a systematic way would have an important bearing on many outstanding biological and geological problems. H. M. D.

Posthumous Stratifications in "Principal" Anhydrite. M. RÓSZA (*Zeitsch. anorg. Chem.*, 1916, **98**, 327—332).—The "principal" anhydrite is the more recent anhydrite of the potash deposits. At Stassfurt this deposit is as much as 80 metres thick. It frequently contains posthumous lenticular and vein-like layers of other salts, analyses of which are given. The changes are partly due to the injection of plastic masses of salts under pressure and partly to chemical transformations. C. H. D.

Presence of Nickel and Cobalt in Chromites. S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1917, **15**, 61—65).—An account of spectroscopic analyses of samples of chromite, some of which contained cobalt and nickel. A. J. W.

Analytical Chemistry.

Simple and Efficient Gas Absorption Apparatus. H. Droop Richmond and E. Hembrough (*J. Soc. Chem. Ind.*, 1917, **36**, 317).—A simple and efficient apparatus for the absorption of gases, such as carbon dioxide, can be made by fitting a tube 13—15 cm. long and about 4 mm. internal diameter, on which six to eight bulbs about 12 mm. in diameter have been blown and the ends of which are expanded into small funnels of about 12 mm. diameter, inside a tube of about 17 mm. internal diameter and 20 cm. long, the bottom of which is drawn out and sealed to an inlet tube of about 3 mm. diameter, bent in the form of a V. In this tube are placed 10—15 c.c. of absorbing liquid. The gas enters through the inlet tube and bubbles up through the bulb tube, passing from bulb to bulb and taking up some of the liquid which overflows from the upper funnel, while fresh liquid continually runs in to replace that carried up; in these circumstances the contact between gas and liquid is efficient. The apparatus is simple, easily made, easily cleaned, and not at all fragile. H. W.

Modern Views of Acid and Alkaline Reactions and their Application to Analysis. I. and II. Niels Bjerrum (*Zeitsch. anal. Chem.*, 1917, **56**, 13—28, 81—95).—I. The author discusses the expression of acid and alkaline reactions in terms of hydrogen-ion concentrations, the theory of indicators, and the influence of indicators on acidimetric estimations.

II. Deals with indicators and the theory of titration. W. P. S.

Estimation of Traces of Water in Alcohol. Nussbaum (*Schweiz. Apoth. Zeit.*, 1917, **55**, 99; from *J. Pharm. Chim.*, 1917, [vii], **15**, 230).—A mixture of equal volumes of absolute alcohol and light petroleum is homogeneous when heated slightly, but becomes turbid when cooled; the point at which the turbidity appears is sharply defined, but is raised by about 16° when the alcohol contains 1% of water. The presence of water in alcohol may therefore be ascertained, and its quantity estimated, by determining the temperature at which the alcohol gives a turbidity when mixed with an equal volume of light petroleum. It is necessary, however, to make preliminary tests with light petroleum and quantities of alcohol containing definite amounts of water, as the point at which the turbidity is observed depends on the kind of light petroleum used. W. P. S.

Catalytic Hydrogenation of Organic Compounds with Base Metals at the Ordinary Temperature. Removal of Halogens from Organic Halogen Compounds. C. Kelber (*Ber.*, 1917, **50**, 305—310. Compare A., 1916, ii, 309, 609).—Details are given of a method for estimating halogens in organic combination, in which the compound is shaken in an atmosphere of hydrogen with

nickel prepared by heating basic nickel carbonate in a current of hydrogen at 310—320°. The medium is either water or dilute alcohol, rendered alkaline. The method appears to have certain advantages over a similar one described by Busch (A., 1916, ii, 534), in which palladinised calcium carbonate is the catalyst. Several analyses are recorded. J. C. W.

Volumetric Analysis of Hypochlorite Solutions used for Sterilising Water. Rapid Analysis of Hydrogen Peroxide. A. Bury (*J. Pharm. Chim.*, 1917, [vii], **15**, 189—195).—The method depends on the reaction between a hypochlorite and hydrogen peroxide according to the equation $NaOCl + H_2O_2 = NaCl + H_2O + O_2$; the volume of the oxygen liberated is equal to that of the chlorine obtained when the hypochlorite is treated with an acid. The reaction may also be used for estimating the strength of hydrogen peroxide solutions. To estimate the available chlorine in a hypochlorite solution, 1 c.c. of the latter is placed in a narrow, graduated tube, which is closed at the bottom and provided with a bulb and tubulure at the top, water is added until the graduated portion of the tube is nearly full, and then hydrogen peroxide up to the zero mark. The tubulure is closed with a rubber stopper carrying a short capillary; the outer end of this is closed with the finger, the tube is inverted, and its contents mixed. When gas ceases to be evolved, the finger is moved slightly to allow the liquid to escape and equalise the pressure, the tube is placed in its normal position, and the volume of the residual liquid noted. The volume of the liquid which has escaped is thus found, and this volume is equivalent to that of the oxygen formed. The tube is graduated so that the readings give directly the quantity of active chlorine per litre of solution. W. P. S.

The Analysis of Gases by means of Orsat's Apparatus, replacing Pyrogallol by Hyposulphites. L. Descamps (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 34—36).—Alkaline pyrogallol can be satisfactorily replaced by a 10% solution of either zinc hyposulphite or sodium hyposulphite, the latter being made slightly alkaline with sodium hydroxide, for the absorption of oxygen. The absorption is rapid and complete after two or three contacts. The presence of a little indigotin in the solution of the sodium salt gives an indication when the reagent requires renewing. W. G.

Estimation of Ozone. David (*Compt. rend.*, 1917, **164**, 430—431).—A rapid method for the estimation of small quantities of ozone in the air or in water. The ozone is made to act on a known volume of $N/100$-ferrous ammonium sulphate solution in dilute sulphuric acid, and this is then titrated back with $N/100$-potassium permanganate solution. It is claimed that by this method 0·02 mg. of ozone can be estimated. The solution of ferrous ammonium sulphate at this dilution is not oxidised by air, even if a large volume of air is bubbled through it, unless ozone is present. W. G.

Use of Diphenylamine and Diphenylbenzidine for Colorimetric Estimations. L. SMITH (*Zeitsch. anal. Chem.*, 1917, **56**, 28—42).—The coloration obtained with diphenylamine in the colorimetric estimation of nitric acid according to Tillmans' method (A., 1911, ii, 151) decreases in intensity when the tube containing the mixture is shaken. It is suggested that a volatile substance is formed by the oxidation of the diphenylamine and that the presence of hydrochloric acid has an influence on the formation of this substance. The stability and intensity of the coloration are at a maximum at the ordinary temperature. The composition of the reagent has an influence on the sensitiveness of the test; for quantities of nitric acid ranging from 0·1 to 3·0 mg. of N_2O_5 per litre the best results are obtained by the use of a reagent consisting of 0·04 gram of diphenylamine, 39 c.c. of water, and 68 c.c. of concentrated sulphuric acid; for from 1 to 25 mg. of N_2O_5 per litre the reagent should consist of 0·08 gram of diphenylamine, 20·5 c.c. of water, and 84 c.c. of sulphuric acid. Diphenylbenzidine behaves similarly to diphenylamine towards nitric acid, but its sensitiveness is about twice as great.

W. P. S.

Prevention of Loss of Ammonia in the Estimation of Nitrogen by Kjeldahl's Method. ALICE WOLF-JOACHIMOWITZ (*Chem. Zeit.*, 1917, **41**, 87).—To prevent loss of ammonia when the acid digestion mixture is rendered alkaline previous to distillation, the sodium hydroxide is added as a concentrated solution which is introduced slowly so that it forms a layer below the acid solution. The two layers are mixed after the flask has been connected with the condenser and absorption apparatus.

W. P. S.

Estimation of Ammonia and Sulphur Compounds in Urine. RICH. WEISS (*Münch. med. Woch.*, 1916, **63**, 1547—1548; from *Chem. Zentr.*, 1917, i, 127. Compare A., 1916, ii, 163). —Malfattis's method of estimating ammonia in urine is recommended for use by physicians, and, for this purpose, a simple apparatus is described. A test-tube is expanded into a bulb at the bottom and etched to indicate 10 c.c. Urine is poured in up to the mark. A few drops of phenolphthalein are added, followed by $N/10$-sodium hydroxide solution until the pink colour is just permanent. The liquid is diluted with distilled water to a second mark, 2—3 drops of phenolphthalein are again added, and, subsequently, exactly neutralised formaldehyde solution (40%) until the liquid reaches a third mark. The red colour disappears; $N/10$-sodium hydroxide is now added until the colour recurs, each c.c. of alkali solution corresponding with 0·0017 gram of ammonia. The tube is graduated in tenths of a c.c. above the upper mark, so that the volume of alkali can be directly determined.

Approximate methods for estimating sulphur compounds in urine are indicated, and an apparatus is described for the determination of pre-formed and total sulphuric acid and of ethyl

hydrogen sulphate. Apparatus for the qualitative and quantitative indentification of indican in urine is depicted. H. W.

Microchemical Detection of Carbon and Sulphur. F. EMICH (*Zeitsch. anal. Chem.*, 1917, **56**, 1—13. Compare A., 1915, ii, 646).—For the detection of carbon in a substance, the latter is heated in a closed capillary in an atmosphere of oxygen and the resulting carbon dioxide is collected in calcium hydroxide solution, the end of the capillary being broken under the surface of this solution when the combustion is completed. The formation of calcium carbonate in the capillary is seen when the latter is observed under the microscope. A distinct reaction can be obtained from 0·0004 mg. of glycerol. Sulphur can be detected by heating similarly small quantities of substance with nitric acid in a closed capillary; the formation of barium sulphate, when the solution is treated with barium chloride, is observed under the microscope. W. P. S.

Estimation of Hardness in Water. ALBRECHT HEYN (*Öff. Gesundheitspflege*, 1916, **7**, 584—604; from *Chem. Zentr.*, 1917, i, 126).—The literature is reviewed and experiments are described which were undertaken with the object of examining the influence of different constituents of natural waters on the estimation of hardness according to the methods of Clark, Winkler, and Wartha-Pfeiffer respectively. It is shown that nitrates, nitrites, and ammonia have no influence. Increase in sodium chloride causes low results for hardness by Clark's method, but has no effect on the other processes. Comparatively large amounts of iron compounds render Clark's method useless, the values obtained being far too high; Winkler's process can scarcely be applied, since it yields low figures for calcium and magnesium, whilst Wartha-Pfeiffer's method easily gives high results. When comparatively large amounts of organic substances are present, Winkler's method is very inexact; the figures for calcium are too high, for magnesium far too low, so that the total hardness is low. Wartha-Pfeiffer's method is also useless, yielding much too high values, particularly in the presence of much magnesium. In general, it appears advisable to determine the carbonate hardness according to Wartha-Pfeiffer, and to estimate calcium and magnesium separately according to Winkler.

The following modified method of calculating the results is proposed: to determine the hardness in degrees, different factors depending on the relative proportions of calcium and magnesium are used instead of multiplying the c.c. of potassium oleate solution used by the factor 0·75 empirically determined by Winkler. When the ratio of the number of c.c. of potassium oleate solution required for the calcium to the number required for the magnesium is 3:1 or over, the volume required for the latter element is multiplied by 0·75; when the ratio lies between 3:1 and 2:1, the factor is 0·6; when under 2:1 it is 0·5. H. W.

Rapid Method for the Estimation of Magnesium. N. BUSVOLD (*Chem. Zeit.*, 1917, **41**, 42).—The following method is

suitable for the estimation of magnesium in limestone. From 5 to 10 grams of the sample are ignited in an electric furnace, cooled, dissolved in the least possible quantity of dilute hydrochloric acid (1 : 1), the solution is boiled, an excess of calcium carbonate is added, the mixture again boiled, filtered, and the insoluble portion washed. The filtrate is treated with 20 c.c. of "6% milk-of-lime," boiled, cooled, filtered, and the precipitate washed with water containing calcium hydroxide. The filter and precipitate are now transferred to a flask and boiled for five minutes with 300 c.c. of water and 40 c.c. of $N/1$-oxalic acid solution; the hot mixture is filtered and the precipitate washed with hot water. The filtrate, which contains magnesium oxalate and free oxalic acid, is cooled, and the free oxalic acid is titrated with $N/5$-sodium hydroxide solution, using methyl-red as indicator. Twenty-five c.c. of dilute sulphuric acid are now added, the solution is heated at 70°, and the total oxalic acid titrated with $N/5$-potassium permanganate solution. The difference between the quantity of total oxalic acid and that of free oxalic acid gives the amount combined with the magnesium; 1 c.c. of $N/5$-oxalic acid solution is equivalent to 0·004306 gram of magnesium oxide. W. P. S.

Electrometric Titration of Zinc with Ferrocyanide. F. Russell von Bichowsky (*J. Washington Acad. Sci.*, 1917, **7**, 141—143).—It is found that the *E.M.F.* of a platinum electrode placed in a solution of potassium ferrocyanide has a value of −0·08 volt; if to such a solution a solution of a zinc salt is slowly added, the *E.M.F.* slowly rises in a normal manner until a quantity of the zinc solution exactly equivalent to the ferrocyanide has been added. When this state is reached, the *E.M.F.* suddenly jumps to −0·40 volt, and remains approximately constant with further addition of zinc. If the process is carried out in the reverse manner, that is, the ferrocyanide is run into the zinc solution, the platinum electrode may have any *E.M.F.* between 0·0 and −0·5 volt, depending on the previous treatment. The reversible value of the platinum electrode of −0·45 volt may be obtained by charging it to 2 volts in a zinc solution. When this initial *E.M.F.* has been obtained the titration cited above may be carried out in the reverse manner, the *E.M.F.* dropping sharply at the end-point to −0·10 volt. J. F. S.

Estimation of Mercury in Organic Compounds. J. E. Marsh and O. G. Lye (*Analyst*, 1917, **42**, 84).—When organic mercury compounds are heated with calcium oxide, as in the ordinary lime-combustion method for the estimation of mercury, the volatilised mercury is frequently contaminated with a tarry or crystalline distillate. This may be prevented by the addition of calcium sulphate to the contents of the combustion tube. The mercury compound should be mixed with about twice its weight of calcium sulphate and an excess of calcium oxide; traces of mercury vapour remaining in the tube at the end of the combustion

may be expelled by a current of carbon monoxide obtained by heating a quantity of calcium oxalate which has been placed previously at the closed end of the tube. W. P. S.

Estimation of Small Quantities of Iron and Aluminium. RAGNAR BERG (*Chem. Zeit.*, 1917, **41**, 50—52).—The method described is particularly intended for the estimation of iron and aluminium in foods and organic substances. After the organic matter has been destroyed by combustion, preferably by heating with sulphuric acid and nitric acid (compare A., 1912, ii, 603), the acid solution containing the mineral substances is rendered alkaline with ammonia, then just acid with hydrochloric acid, a small quantity of ammonium acetate is added, the solution boiled, and the precipitate collected and washed with hot, very dilute ammonium sulphate solution. The precipitate is dissolved in hydrochloric acid, again precipitated as described, then dissolved once more in hydrochloric acid, the solution rendered ammoniacal, boiled, and the precipitate, consisting of iron and aluminium phosphates and silica, is collected, washed, ignited, and weighed. The silica is separated by fusion with potassium hydrogen sulphate, collected, and weighed; the solution containing the iron and aluminium phosphates is treated with ammonia, the precipitate obtained collected and washed, then dissolved in hydrochloric acid, the solution is transferred to a stoppered flask, zinc chloride added, the mixture is rendered alkaline with sodium hydroxide, then slightly acid with hydrochloric acid, and potassium iodide is added. The mixture is heated at 65° for twenty minutes, and the liberated iodine then titrated with $N/250$-thiosulphate solution. One atom of iodine is equivalent to 1 atom of iron. The aluminium is found by difference. W. P. S.

Estimation of Small Quantities of Cobalt. A. D. POWELL (*J. Soc. Chem. Ind.*, 1917, **36**, 273—274).—Cobalt may be estimated by taking advantage of the fact that cobalt ammonium thiocyanate forms an intensely blue solution in amyl alcohol; in the presence of iron, the blue colour is masked by the red colour of ferric thiocyanate and the solution must be shaken with sodium carbonate or hydroxide to destroy the ferric salt, when the blue colour of the cobalt salt becomes apparent.

The author has applied this method to the estimation of cobalt in samples of pyrolusite containing 2% or more of iron oxide, and finds that the minimum concentration of ammonium thiocyanate necessary for complete extraction of cobalt is 25%; with lower concentrations, either the cobalt is not extracted from the aqueous solution by the amyl alcohol or, after extraction with the iron, the addition of sodium carbonate and consequent reduction in the concentration of the ammonium thiocyanate causes part of the cobalt to be re-extracted into the aqueous solution. A further difficulty is encountered in clarifying the amyl-alcoholic extracts previous to matching the colours; filtration through paper is inadmissable, as

the colour is absorbed to a considerable extent and, even after long keeping, the extracts always contain sufficient ferric hydroxide in suspension to give a green shade. The trouble can be avoided by substituting sodium pyrophosphate for the sodium carbonate, except in cases in which manganese is present in such amount that the precipitate of manganese pyrophosphate renders extraction impossible.

The method thus modified has the advantages that the cobalt can be directly extracted, since the iron does not react with the thiocyanate if about half a gram of sodium pyrophosphate is present, and, further, that the extracts have a very uniform colour which remains unchanged during many months if the solution is kept in contact with a little sodium pyrophosphate. H. W.

Estimation of Nickel in the Presence of Zinc and Iron. S. Rothschild (*Chem. Zeit.*, 1917, **41**, 29—30).—Nickel cannot be deposited electrolytically from an ammoniacal solution with any degree of success when zinc or much manganese is present, although the process is trustworthy when the solution contains only iron and aluminium in addition to the nickel; deposition of nickel from a hot solution in the presence of sodium sulphite is untrustworthy in the presence of cobalt. Small quantities of iron are precipitated with the nickel when the latter is separated by means of dimethylglyoxime, and this contamination with iron is not prevented by the addition of a relatively large quantity of tartaric acid. It is therefore recommended that the nickel be precipitated in the usual way with dimethylglyoxime, the precipitate then dissolved in hydrochloric acid, the solution boiled for a few minutes with the addition of hydrogen peroxide, treated with an excess of ammonia, and the nickel deposited electrolytically from the solution. W. P. S.

Estimation of Chromium in Ferrochrome, Steel, and Slags by the Permanganate Method. P. Koch (*Chem. Zeit.*, 1917, **41**, 64).—About 0·25 gram of the finely divided sample is fused for twenty minutes in a porcelain crucible with 4 grams of sodium peroxide; when cold, the mass is boiled with water for thirty minutes, or until all the excess of peroxide has been decomposed; the mixture is then cooled, the ferric hydroxide is dissolved by the addition of sulphuric acid, excess of standardised ferrous sulphate solution is added, and this excess then titrated with permanganate solution. The ferrous sulphate solution may be standardised against $N/10$-potassium dichromate solution (4·9033 grams of the salt per litre), each c.c. of which is equivalent to 0·001733 gram of chromium. W. P. S.

Estimation of Small Amounts of Sugar in Urine. V. C. Myers (*Proc. Soc. Exper. Biol. Med.*, 1916, **13**, 178—180; from *Physiol. Abstr.*, 1916, **1**, 354).—Creatinine, uric acid, and probably other interfering substances, are precipitated with picric acid,

as suggested by Folin; after that, a technique similar to that introduced by Benedict and Lewis for the estimation of sugar in the blood is employed. Full details of the method are given. Normal urine contains from 0·08—0·2% sugar. G. B.

Estimation of Sugar. N. SCHOORL and (MEJ.) A. REGENBOGEN (*Chem. Weekblad*, 1917, **14**, 221—229).—A reply to the criticisms of Ruoss (A., 1916, ii, 155) on the Fehling process for estimating sugars. The authors find that these substances can be satisfactorily estimated by the iodometric method of back-titration.
A. J. W.

The Influence of Pentoses in the Estimation of Reducing Sugars by means of the New Method of Heating at 63—65° for Ten Minutes (Mixture of the Cupropotassic Solution and the Liquid to be Analysed). H. PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 21—24).—The pentoses, arabinose and xylose, both reduce the alkaline copper tartrate solution under the experimental conditions, but it is necessary to prolong the heating to forty minutes for the reduction to be complete. Where the pentoses are present, it is advisable to follow the method of Maquenne (compare A., 1916, ii, 156) and do trial estimations, always having the same amount of sucrose present. Another portion of the liquid is fermented, the sucrose and reducing sugars being destroyed, and the pentoses left are estimated directly. It is advisable for each analyst to fix his own conditions and prepare his own tables showing the values of differing amounts of each sugar in terms of copper or copper oxide under these conditions.
W. G.

The Estimation of Reducing Sugars in Sugar-cane Molasses and in the Fermented Liquid of these Molasses for the Estimation of the Fermented Sugars. H. PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 24—28. Compare preceding abstract).—The author advocates the use of his method of estimating reducing sugars, by carrying out the reduction at 63—65° for ten minutes, claiming that, under these conditions, the action of the organic substances present is so diminished as to permit of the use of 1 gram of molasses for the direct estimation and 5 grams of the molasses after fermentation. W. G.

Muller's Process for the Destruction of Reducing Principles, permitting of the Direct Estimation of Crystallisable Sugar, specially applicable to the Products of the Cane-sugar Industry. CH. MULLER (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 28—32).—The method is based on the use of Nylander's reagent (alkaline bismuth tartrate). Fifty c.c. of the sugar solution are heated on a water-bath for fifteen minutes with 5 to 15 c.c. of the reagent, according to the amount of reducing substances present. The liquid is cooled, 60 c.c. of basic lead

acetate solution are added, the whole is made up to 300 c.c., shaken, filtered, and polarised in a 300 mm. tube. To 100 c.c. of the liquid 10 c.c. of 50% acetic acid are added, and the liquid again polarised. The liquid can be decolorised if necessary before polarisation. If more than 3 grams of reducing substances are present, proportionately more of Nylander's reagent must be added. The results obtained by this method are in close agreement with those from the longer and more complicated methods commonly used. W. G.

Glutose. H. PELLET (*Ann. Chim. anal.*, 1917, **22**, 43—47).—This carbohydrate is not fermented by yeast, and its quantity in molasses may be estimated by fermenting all the other sugars present and then taking the reducing power of the solution. One hundred grams of the molasses are diluted to 600 c.c., 1·5 c.c. of sulphuric acid added, then 50 grams of bottom fermentation yeast mixed with water, the whole mixture is diluted to 1 litre, and allowed to ferment for seventy-two hours. A portion of the solution is then treated with normal lead acetate, excess of lead is removed by the addition of sodium carbonate, and the cupric reducing power is estimated. The mixture of the Fehling solution and the solution under examination is heated at 65° for thirty minutes, the cuprous oxide then collected, dried, and weighed. The factor 1·008 is used to convert the weight of cuprous oxide found into glutose; the latter has about one-half the cupric reducing power of invert sugar. Sugar-cane molasses contain from 2·60 to 5·60% of glutose. W. P. S.

Qualitative Analysis of Carbohydrate Mixtures. J. M. KOLTHOFF (*Pharm. Weekblad*, 1917, **54**, 205—214).—A scheme for the detection of sucrose, lævulose, dextrose, lactose, dextrins, gums, amylum, and cellulose in mixtures of these substances. A. J. W.

Polarimetric Estimation of Starch in the Presence of other Optically Active Substances. C. BAUMANN and J. GROSSFELD (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 97—103).—The method described is particularly useful for the estimation of starch in products which contain starch paste, dextrins, and sugars, and depends on the fact that starch, whether raw or heated, is precipitated completely by lead tannate when the latter is formed in the starch solution. Ten grams of the substance under examination are shaken for 15 minutes (or for 1 hour if dextrins are present) in a 100 c.c. flask with 75 c.c. of water; 5 c.c. of 10% tannin solution are then added, followed by 5 c.c. of basic lead acetate solution, and the mixture is diluted with sodium sulphate solution to 100 c.c. After filtration, 50 c.c. of the clear filtrate are mixed with 3 c.c. of 25% hydrochloric acid and heated for 15 minutes in a boiling water-bath, then cooled; 20 c.c. of 25% hydrochloric acid and 5 c.c. of sodium phosphotungstate solution (12 grams of sodium phosphate and 20 grams of sodium tungstate per 100 c.c.) are added,

the mixture is diluted to 100 c.c., filtered, and polarised in a 200 mm. tube. Another portion of 5 grams of the sample is heated directly with hydrochloric acid (compare Ewers' method, A., 1908, ii, 543) and the solution polarised after the addition of a further 20 c.c. of hydrochloric acid and clarification with sodium phosphotungstate. The difference between the two polarimeter readings is multiplied by 5·444 to obtain the percentage quantity of starch present; this factor is calculated from the average rotatory power of various starches, the average being $[\alpha]_D = +183 \cdot 7^\circ$. On account of the presence of acetates in the first part of the process, it is necessary to add 3 c.c. of hydrochloric acid, instead of 2 c.c. as given by Ewers, to bring the acidity of the mixture to the required concentration; the additional quantity of hydrochloric acid introduced after the inversion is for the purpose of insuring the complete precipitation of organic bases, alkaloids, etc., which may be present; sodium phosphotungstate fails to effect their entire removal from the more dilute hydrochloric acid solution. The error of the method does not exceed 0·2% when dealing with substances containing from 10 to 60% of starch together with large proportions of sucrose, dextrose, dextrins, milk, etc. W. P. S.

Analysis of Aspirin. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], **15**, 213—222).—The presence of acetic acid in the aspirin (*o*-acetoxybenzoic acid) molecule may be ascertained by treating the substance with an excess of calcium hydroxide, separating the insoluble calcium salicylate by filtration, and applying the usual tests for acetic acid to the residue obtained on evaporating the filtrate; it is necessary to ignite this residue at a low temperature in order to destroy remaining traces of salicylate before the tests are applied. Aspirin should not give a coloration with ferric chloride (absence of free salicylic acid), and should volatilise completely when heated. It should melt at 132°; in determining the melting point, the bath should be heated at about 125° before the capillary containing the substance is introduced, since aspirin tends to decompose and give a false m. p. when heated for some time at a temperature above 100°. To estimate the quantity of aspirin present in a sample, the acid and saponification numbers should be determined (compare Astruc, A., 1913, ii, 806). Samples of so-called aspirin examined by the author consisted of magnesium sulphate 53%, lactose 39%, and *o*-acetoxybenzoic acid and salicylic acid 8%. W. P. S.

Soluble Filters and Filtering Media. JOHN M. WILKIE and H. S. ANDERSON (*J. Soc. Chem. Ind.*, 1917, **36**, 272—273).—The use of soluble filters is discussed, the term being applied to filters in which both the medium and medium support are soluble in some arbitrarily selected liquid. For the separation of potash soaps from strong alcoholic mother liquors, a filter prepared as described below has proved very serviceable. A pear-shaped separator of 150—200 c.c. capacity is selected with a well-marked

tubular portion between bulb and stopcock. Special potassium nitrate crystals are introduced, so as to give a column nearly filling the tube, and then 3—5 grams of powdered potassium nitrate which has been rubbed down smooth between paper just previous to use. The separator is finally tapped on the bench to consolidate the filter. The filter is then ready for use, and with alcoholic soap solutions no precautions are required other than seeing that the added liquor does not unduly disturb the surface of the potassium nitrate powder. In place of potassium nitrate, ammonium chloride may be used. H. W.

Estimation of the Alkaloids by Physico-chemical Volumetric Methods. PAUL DUTOIT and MEYER LÉVY (*J. Chim. phys.*, 1916, **14**, 353—360).—The application of electrical conductivity measurements is recommended as furnishing a satisfactory method for the estimation of alkaloids. The method may be applied in several forms, according to whether the free alkaloid is neutralised by addition of an acid, or is displaced from its salts by the addition of a strong base, or is precipitated by the addition of one or other of the characteristic alkaloid reagents.

The first method is not of any real practical importance, but the second has been found to give quite satisfactory results with a number of alkaloids. Of the various specific alkaloid reagents which have been examined in connexion with the third method, the best results were obtained with silicotungstic acid. This acid is quite stable, and its conductivity remains constant even in very dilute solution. In applying the conductivity method with the use of silicotungstic acid to the estimation of alkaloids, the method followed is to add sodium acetate to the solution of the alkaloid salt, the concentration of which should be of the order $N/100$ to $N/1000$, the conductivity of the solution being then measured. Successive quantities of $N/2$- to $N/20$-solution of silicotungstic acid are then added, and the conductivity measured after each addition. The quantity of sodium acetate added should be such as to make its molar concentration from two to three times that of the alkaloid. The conductivity data when plotted give two intersecting curves, the point of intersection corresponding with the complete precipitation of the alkaloid. In most cases this is attained when the ratio of alkaloid to silicotungstic acid is as 4:1. H. M. D.

Colorimetric Estimation of Creatinine. L. GERET (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 35—38).—The modification of the picric acid method described by Baur and Trümpler (A., 1914, ii, 595) yields about 33% more total creatinine than is found by the older method given by Baur and Barschall, and this difference in the quantities of creatinine found by the two methods does not therefore indicate that the quality or method of preparation of standard meat extracts have altered. W. P. S.

Identification of Opium with the Aid of Meconine and Meconic Acid. O. TUNMANN (*Apoth. Zeit.*, 1916, **31**, 499—500; 503—504; from *Chem. Zentr.*, 1917, i, 131—132).—Zinc chloroiodide is a suitable reagent for the microchemical detection of opium in broken pieces and dust; when the preparation is gently warmed with the reagent, the polygonal epidermal cells of the poppy capsule are well defined, the secondary membranes being coloured violet-blue, the primary deep yellow.

The meconic acid content of opium may fall as low as 1·5%. In using Autenreith's method of testing for meconic acid, it is necessary to filter the solution of magnesium meconate at the boiling point. In addition, it is frequently advisable to decolorise the aqueous solution of the residue obtained from the alcoholic extracts by means of benzene previous to boiling with magnesium carbonate. The maximum meconin content in opium in seven cases investigated was 0·112%. Little reliance can be placed on the sulphuric acid test for meconin.

The copper, silver, ferrous, and pyridine salts of meconic acid are suitable for its microchemical detection. The copper salt forms 3—5—10 μ long, pale yellow, intermingled needles and rods with occasional nodules. Limit of sensitiveness, 40—50 μg. In spite of their smallness, the crystals shine brightly between crossed Nicols. The silver salt appears under the microscope as yellow, occasionally almost black, needles (diameter, 15—25 μ) grouped in clusters, less frequently as colourless crystals, of length up to 20 μ. In polarised light, the smaller nodules show a dark cross, the larger groups appear grey and greyish-brown. Extinction in the single crystals is parallel to the long axis. The limit of sensitiveness is 5μg. The ferrous salt is prepared by adding a grain of dehydrated ferrous sulphate to a drop of meconic acid; the mixture is warmed until a pale red solution is formed. After five to ten minutes, the formation of reddish-brown nodules and single crystals is observed, the latter gradually forming aggregates. All the crystals glow red in polarised light and show strong pleochroism. Limit of sensitiveness, 15—20 μg. The pyridine salt forms long, fine, colourless, single, prismatic needles, occasionally grouped in sheaves; the mean length of the needles is 60—120 μ and mean breadth 2·3 μ. Between crossed Nicols they appear pale grey. Limit of sensitiveness, 50 μg. Lastly, the reactions with zinc chloroiodide, potassium bismuth iodide, and potassium iodide–iodine can be used. The former yields a yellow, amorphous precipitate, whilst the other reagents give yellow or yellowish-brown nodules and sun-like crystal aggregates which, with the last-named reagent, attain a diameter of 300—400 μ. H. W.

Estimation of Antipyrine. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], **15**, 97—105).—A volumetric process described by Bougault (A., 1899, ii, 193) for the estimation of antipyrine depends on the titration of the substance in alcoholic solution with iodine solution in the presence of mercuric chloride; this method is trustworthy provided that the iodine solution is standardised

against pure antipyrine at the time it is used. Bougault has also stated (A., 1900, i, 312) that the weight of the precipitate of iodo-antipyrine (which is formed when antipyrine in dilute sodium acetate solution is treated with iodine solution) is an approximate measure of the quantity of antipyrine present, but does not claim that the reaction is quantitative. The author finds that this gravimetric method is untrustworthy, although it has been adopted by the French Codex in preference to the volumetric method.

W. P. S.

Biochemistry of Tobacco. I. Critical Examination of the Methods of Estimating Nitrogenous Substances in Tobacco Leaves. G. Paris (*Staz. sperim. agrar. ital.*, 1916, **49**, 405—424; from *Chem. Zentr.*, 1916, ii, 1079—1080).—An examination of the most important methods given in the literature has shown that the ammonia-nitrogen is not completely precipitated by phosphotungstic acid in sulphuric acid solution, but is partly contained in the amino-nitrogen estimated by difference. Similarly, the general methods of estimating amino- and protein-nitrogen yield inexact results. The volumetric estimation of nicotine is accurate if certain precautions are taken. The following methods are proposed: Water, total nitrogen, and nicotine are estimated in the tobacco itself, total nitrogen, protein nitrogen, nicotine nitrogen, ammonia nitrogen, nitric acid nitrogen, and amino-nitrogen in the aqueous extracts. The latter are obtained by agitation for six hours with water at 30—35°. Total nitrogen is estimated according to Kjeldahl, nicotine by Bertrand and Javillier's method (by precipitation as silicotungstate and weighing the silica and tungsten oxide after igniton, etc.), soluble protein-nitrogen according to Stützer, ammonia-nitrogen by distillation under diminished pressure, nitric acid nitrogen by Schlœsing-Wagner's method. For the estimation of amino-nitrogen, the protein nitrogen in the extract is removed by basic lead acetate, the filtrate freed from lead by sulphuric acid, and the bases precipitated by phosphotungstic acid (10%), care being taken to avoid any excess. A portion of the filtrate is freed from sulphuric and phosphotungstic acids by means of baryta; the solution is made up to a definite volume and filtered; after removal of excess of baryta with carbon dioxide the filtrate is concentrated to 50—60 c.c. at a low temperature, care being taken to maintain neutrality by periodical addition of very dilute nitric acid. The solution is finally precipitated by freshly prepared, clear mercuric nitrate solution, an excess of the reagent being avoided. The precipitate is filtered, decomposed with sulphuric acid according to Kjeldahl, and the nitrogen estimated. The filtrate from the mercury precipitate contains traces of asparagine and other amides and aspartic acid which have escaped precipitation. It can be made alkaline and the liberated ammonia distilled under diminished pressure.

H. W.

Detection of Albumin in Urine. Aufrecht (*Pharm. Zeit.*, 1917, **62**, 38).—Ten c.c. of saturated sodium chloride solution,

acidified previously with a few drops of concentrated nitric acid, are placed in a test-tube, and the urine to be tested is poured on the surface of this solution; if albumin is present, a turbid ring forms at the junction of the two liquids. The test will detect the presence of as little as 0·01 gram of albumin per litre of urine.

W. P. S.

The Detection of Blood, especially by means of Malachite-green, and a New Test with Rhodamine. E. FULD (*Biochem. Zeitsch.*, 1917, **79**, 241—256).—The author gives a review of the various methods for detecting blood (in fæces, etc.) by means of guaiacum tincture, reduced solutions of malachite-green, phenolphthalein, etc. He finds as specially sensitive a reagent made from rhodamine B extra, prepared by dissolving 0·2 gram of the dye in 50 c.c. alcohol, adding 5 grams of zinc dust and 4 c.c. of 10% sodium hydroxide to the boiling alcoholic solution. Such a solution, on the addition of 3% hydrogen peroxide, gives a coloration with blood in a dilution of 1 in 10,000,000, and is much more sensitive than a solution produced by the reduction of malachite-green.

S. B. S.

Electrometric Method of Titration, and its Application to the Examination of Gastric Juices. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1917, **79**, 1—34).—For the purposes of titration, a special form of electrode is figured and described. It consists essentially of a tube ending in a glass bell, into the side of which is fused another tube containing mercury having a platinum wire fused into the lower end, which just dips under the liquid to be titrated. Into the former tube hydrogen is passed. Connexion is made between the liquid to be titrated and the other half-cell through an inverted test-tube containing a gel of saturated potassium chloride solution with 3% agar. This is connected with a saturated solution of potassium chloride, which in its turn is connected with the calomel half-electrode. A large number of curves are given representing the changes in the [H˙] concentration when solutions of various acids and mixtures of acids are titrated with $N/10$-sodium hydroxide. Similar curves are given to show corresponding changes when gastric juices are titrated, and the results are correlated with the changes in colours of indicators and the reaction of gastric juices towards Günzberg's reagent. As a result of the experiments, the author recommends the following methods of analysis of gastric juices: I. For exact analysis, (*a*). For estimation of free hydrochloric acid, the electrometric measurement of [H˙] in the juice. (*b*) For estimation of bound hydrochloric acid, either chemical methods or electrometric titration to the point $p_4 = 6·5$. II. For approximate clinical methods, the following three titrations: (*a*) to the salmon-pink tint with dimethylaminoazobenzene; (*b*) to the citron-yellow colour of the same indicator; (*c*) to the change in phenolphthalein. S. B. S.

General and Physical Chemistry.

Refractometry of Solutions. LUCRECIA M. BLANC (*Ann. Soc. Quim. Argentina*, 1916, **4**, 294—314).—The index of refraction of solutions of the chlorides, sulphates, and nitrates of ferric iron, chromium, cobalt, nickel, and manganese increases regularly with the concentration. A. J. W.

Phototropic Phenomena of the Sulphates of Strontium, Calcium, and Barium. JOSÉ RODRÍGUEZ MOURELO (*Anal. Fis. Quim.*, 1917, **15**, 74—93).—An account of the influence of varying proportions of manganese and bismuth on the phototropic and phosphorescent properties of the sulphates of the alkaline-earth metals. A. J. W.

Triboluminescence. A. IMHOF (*Physikal. Zeitsch.*, 1917, **18**, 78—91).—The phenomenon of triboluminescence has been examined in experiments with a large number of substances, the object in view being to ascertain the influence of the size of the crystals, of temperature, and water of crystallisation, and also of the chemical relations.

For a particular triboluminescent substance, the emission of light can only be observed if the size of the crystals exceeds a certain limiting value. This varies from 0·002 to 4 mm., according to the nature of the substance, the limiting size decreasing with increase in the intensity of the triboluminescent emission. This intensity decreases for the most part with rise of temperature, but some observations at $-80°$ indicate that there is a maximum on the intensity–temperature curve for certain substances between this and the ordinary temperature. The influence of temperature varies considerably with the nature of the substance. Triboluminescence is still exhibited by phosphorescent substances when the temperature has been raised sufficiently high to inhibit the phosphorescent emission.

In addition to eighty-seven inorganic substances, 25% of which were found to be triboluminescent, the effect was also investigated in a number of minerals and amorphous substances. The results seem to show that triboluminescence is not shown by the elements. Amongst compounds, chemically related substances behave similarly in regard to the phenomenon. When the various crystalline hydrates of a particular substance are compared, it is found that the behaviour depends on the water content. For the most part, the highest hydrate shows triboluminescence, whereas lower hydrates are inactive, but there are exceptions to this rule.

The spectral character of the triboluminescent radiation has been examined in a large number of cases. The emitted light is blue in the case of about 50% of the substances examined and yellow or orange for about 25%. The colour varies to some extent with the temperature, the wave-length sometimes increasing and sometimes decreasing as the temperature rises. H. M. D.

Effect of Various Substances on the Photochemical Oxidation of Solutions of Sodium Sulphite. J. HOWARD MATHEWS and (MISS) MARY ELVIRA WEEKS (*J. Amer. Chem. Soc.*, 1917, **39**, 635—646).—The influence of a number of substances on the photochemical oxidation of $0\cdot2N$-solutions of sodium sulphite at 26° by ultra-violet light has been carefully examined. The reactions took place in quartz flasks, which were placed in a thermostat at fixed distances from the mercury lamp and constantly fed with air and stirred. A control reaction was carried out alongside the reaction under investigation. It is shown that copper sulphate has no appreciable effect on the velocity, pyridine strongly inhibits the reaction; methyl acetate and ethyl acetate also inhibit the reaction, but to a much smaller extent. Benzaldehyde, quinol, phenol, quinine sulphate, sucrose, and glycerol all inhibit the reaction, whilst carbamide has practically no effect whatever. The action of quinol decreases as the action proceeds, probably due to the decomposition of it by the light. Curves of the whole of the reactions with those of the accompanying controls are given in the paper.

J. F. S.

A Comparison of Radium Standard Solutions (continued). J. MORAN (*Trans. Roy. Soc., Canada,* 1916, [iii], **10**, 77—84. Compare A., 1915, ii, 726).—The deterioration of the standards with repeated use is now ascribed to faulty experimentation, and the regeneration of deteriorated standards by addition to hydrochloric acid to the unsuspected presence of radium in the acid. In a new set of determinations, in which attention was paid to sources of error, no deterioration of the standards with use occurred. The Rutherford–Boltwood standards were found, in terms of the Washington standard, to be 96·4% for the weak and 97·3% for the strong.

F. S.

Attempt to Separate the Isotopic Forms of Lead by Fractional Crystallisation. THEODORE W. RICHARDS and NORRIS F. HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 531—541).—Lead from Australian carnotite, containing 1 part of ordinary lead, 3 parts of radium-*G*, and a trace of radium-*B*, has been fractionally crystallised more than one thousand times as nitrate. The end fractions, least soluble and most soluble, were then purified and used for the determination of the atomic weight of the metal by means of the ratio $PbCl_2:Ag$. The following values were obtained: Pb (least soluble fraction) = 206·422; Pb (most soluble fraction) = 206·409. These values, it will be seen, agree to within 6 parts per 100,000, an amount which is inside the limits of experimental error. The β-ray activity of both end-fractions was also determined, and the values obtained agreed to within the experimental error of 1%. These observations indicate that the nitrates of radium-*D* and lead on the one hand and radium-*B* and lead on the other could scarcely be separated, if at all, by less than 100,000 crystallisations. Hence it may be inferred that the molecular solubilities of the nitrates are probably essentially identical. The outcome of the

experiments gives strong experimental evidence in support of the hypothesis that isotopes are really inseparable by any such process as crystallisation. J. F. S.

The Explosive Potential in Carbonic Anhydride at High Pressures. CH. EUG. GUYE and C. STANESCU (*Compt. rend.*, 1917, **164**, 602—605).—The authors deduce the expression $V=F(m.d)$ for the value of the explosive potential in terms of m, the number of molecules in unit volume of the gas, and d the distance between the plates between which the discharge vibrates. This formula is verified for carbon dioxide at the ordinary temperature, with pressures varying between five and forty-five atmospheres and for distances between 0·34 mm. and 2·24 mm. The expression $V=F(m.d)$ thus applies to a gas compressed within limits much wider than those allowed by the Mariotte–Gay Lussac law. W. G.

Disruptive Discharge in Compressed Gases. CH. EUG. GUYE and C. STANESCU (*Arch. Sci. phys. nat.*, 1917, **43**, 131—160).—A fuller account of work already published (compare preceding abstract). W. G.

Ion Adsorption Potentials. EMIL BAUR and S. KRONMANN (*Zeitsch. physikal. Chem.*, 1917, **92**, 81—97).—In a previous paper (*Zeitsch. Elektrochem.*, 1913, **19**, 590) measurements were recorded of potential differences at the surface of contact of aqueous and non-aqueous solutions, which were attributed to the adsorption of ions at the surface. Further measurements have now been made of the *E.M.F.* of cells in which two equally concentrated aqueous solutions of an electrolyte are separated by a non-aqueous liquid layer, a second electrolyte being added to one of the aqueous solutions. The cells examined were arranged according to the scheme:

$$N.E.|0{\cdot}01N\,\mathrm{KCl}|A|B+0{\cdot}01N\,\mathrm{KCl}|N.E.,$$

in which $N.E$ represents the normal electrode, A amyl alcohol which was chiefly used as the non-aqueous liquid, and B the foreign electrolyte, which consisted of sodium or potassium picrate or strychnine sulphate or chloride.

In consequence of diffusion, the *E.M.F.* of such cells changes with time, and this effect, as well as the influence of the concentration of the added picrate or strychnine salt, has been examined in detail. The general behaviour of cells of this type is quite consistent with the view that the contact potentials are due to the adsorption of picrate or strychnine ions. In particular, it is found that the relation between the *E.M.F.* and the concentration of the adsorbed ions in the solution is in agreement with the requirements of the adsorption formula. H. M. D.

Standard Cells and the Nernst Heat Theorem. F. M. SEIBERT, G. A. HULETT, and H. S. TAYLOR (*J. Amer. Chem. Soc.*, 1917, **39**, 38—52).—The authors have determined the specific heats of $CdSO_4,8/3H_2O$ and $CdCl_2,5/2H_2O$ over the temperature range

87° abs. to 274° abs., with the object of completing the data necessary for testing the Nernst heat theorem on the two standard cells, Cd(amalgam) | $CdSO_4$,8/3H_2O,Hg_2SO_4 | Hg and Cd(amalgam) | $CdCl_2$,5/2H_2O,Hg_2Cl_2 | Hg. The apparatus employed in the determinations and the method adopted were essentially the same as those of Nernst and Schwers (A., 1914, ii, 336). The experimentally determined values are expressed as functions of the temperature, the function being obtained with the aid of the Nernst–Linnemann specific heat equation. The values have been utilised along with other data obtained from the literature to investigate the thermodynamic relationships of the above-mentioned cells. Satisfactory agreement has been obtained between the calculated and the observed values with the assumption of Nernst for condensed systems and the consequent deduction that the integration constant in the thermodynamic equation is equal to zero. J. F. S.

Electromotive Force Developed in Cells containing Non-aqueous Liquids. J. M. Nelson and W. V. Evans (*J. Amer. Chem. Soc.*, 1917, **39**, 82—83).—An account is given of some preliminary experiments which tend to show that the solution of a metal in acid is first preceded by the formation of an additive compound similar to the Grignard compounds. It is shown that the addition of magnesium ethyl bromide lowers the electrical resistance of ethyl ether and ethyl ether–benzene mixtures from 1×10^7 ohms to 9×10^2 ohms. The *E.M.F.* of cells of the type Mg | ether + C_2H_5Br + C_2H_5MgBr | Pt varies between 0·5 and 1·5 volts, whereas cells Mg | ethyl ether + C_2H_5Br | Pt could not be shown to possess any *E.M.F.* when first formed, but after keeping for some time an *E.M.F.* was set up due to the formation of the Grignard compound. Similar experiments were conducted with zinc and aluminium electrodes in place of magnesium, and instead of adding the Grignard compound a trace of iodine was added. Under these conditions each of these metals behaved exactly like magnesium. J. F. S.

The Absence of Thermal Hysteresis in the Copper-Constantan Thermo-element between 30° and 100°. T. W. Richards and H. W. Richter (*J. Amer. Chem. Soc.*, 1917, **39**, 231—235).—It has been found that a highly sensitive copper–constantan multiple thermo-element shows no appreciable thermal hysteresis when subjected to rapid changes of temperature between 30° and 100°. The instrument is accordingly well adapted for certain types of accurate thermometric work. H. M. D.

The Application of the Theory of Allotropy to Electromotive Equilibria. III. Consideration of the Solubility of Metal and Electrons. A. Smits and A. H. W. Aten (*Zeitsch. physikal. Chem.*, 1917, **92**, 1—34. Compare A., 1916, ii, 77).—An account of the authors' views which have been for the most part published previously elsewhere (A., 1916, ii, 410, 597). H. M. D.

Applicability of the Ferro-Ferricyanide Electrode to the Measurement of the Activities of Electrolytes in Concentrated Solutions. G. A. LINHART (*J. Amer. Chem. Soc.*, 1917, **39**, 615—621).—A number of *E.M.F.* measurements of the ferro-ferricyanide electrode containing various concentrations of the two salts and various concentrations of potassium chloride (Linhart, this vol., ii, 13) against calomel electrodes have been made at 25°. It is shown that for given concentrations of potassium chloride the activities of the potassium ferro- and ferri-cyanides are proportional to their total concentrations. Concordant E_0 values are obtained by substituting the experimental values and those of Lewis and Sargeant (A., 1909, ii, 369) in the equation:

$$E_{obs.} = E_0 - 0{\cdot}05914 \log \{(K_4Fe[CN]_6)/(K_3Fe[CN]_6)(K^{\cdot})(Cl')\},$$

for concentrations of potassium chloride between $0{\cdot}2N$ and saturation, provided the approximately correct activity product of potassium and chloride ions is used. It is pointed out that since the E_0 values are fairly concordant for a definite range of concentration of electrolyte, the ferro-ferricyanide electrode can be used as a reference electrode for measuring activity products of many electrolytes. In addition to the measurements of activity products of simple ions, further work is contemplated on multivalent ions.

J. F. S.

Adsorption and Ionisation Equilibria. A. REYCHLER (*Kolloid Zeitsch.*, 1917, **20**, 81—83).—The Storch formula expressing the relation between the degree of ionisation of a strong electrolyte and the concentration of the solution is of the same type as the adsorption formula. It is suggested that this formal analogy may be an expression of the existence of some relation between the ionisation process and the adsorption of the ions and the non-ionised molecules of the electrolyte by the solvent.

H. M. D.

Correlation of Ionisation and Structure in Unsaturated Acids. C. G. DERICK and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1917, **39**, 388—398).—The equivalent conductivities and ionisation constants of eight monocarboxylic naphthalene derivatives have been determined at 25° and the following values obtained: β-Naphthoic acid, $K_a = 6{\cdot}81 \times 10^{-5}$; Δ^1-dihydro-β-naphthoic acid (m. p. 118·5°), $K_a = 2{\cdot}91 \times 10^{-5}$; Δ^2-dihydro-β-naphthoic acid (m. p. 161°), $K_a = 2{\cdot}54 \times 10^{-5}$; Δ^3-dihydro-β-naphthoic acid (m. p. 101·2°), $K_o = 5{\cdot}70 \times 10^{-5}$; *ac*-tetrahydro-$\beta$-naphthoic acid (m. p. 96°), $K_a = 2{\cdot}45 \times 10^{-5}$; Δ^1-dihydro-α-naphthoic acid (m. p. 121·5°), $K_a = 7{\cdot}89 \times 10^{-5}$; Δ^2-dihydro-α-naphthoic acid (m. p. 86°), $K_a = 11{\cdot}44 \times 10^{-5}$; and *ac*-tetrahydro-$\alpha$-naphthoic acid (m. p. 85°), $K_a = 4{\cdot}40 \times 10^{-5}$. The place influence for a double bond in the Δ^2-position in respect to the carboxyl group has been shown to be a constant for the cyclic acids. Attention is directed to the dangers of drawing conclusions from the ionisation constants of unsaturated fatty acids where cis-trans-isomerism, due to the double bond, is possible. The

place influence for a Δ^1 double bond has been shown to vary with the degree of conjugation, and it is suggested that a quantitative interpretation of Thiele's partial valency theory may be developed from this point of view. J. F. S.

Abnormal Electrolytic Dissociation. A. N. SACHANOV (*J. Physical Chem.*, 1917, **21**, 169—189).—The influence of concentration on the electrical conductivity of silver nitrate dissolved in liquids of varying dielectric capacity is discussed in reference to data previously published (A., 1915, ii, 729, 730). These data lead to the conclusion that the molecular conductivity, after correction for viscosity, shows a minimum at a certain concentration in all solvents. This concentration is largely determined by the dielectric capacity of the solvent, and increases with the magnitude of the dielectric constant. In proceeding from very dilute solutions, the molecular conductivity decreases at first with increasing concentration, reaches the minimum referred to above, and then increases as the concentration is further increased. This part of the conductivity–concentration curve corresponds with the so-called abnormal ionisation, which is attributed to the polymerisation of the electrolyte and the ionisation of the complex molecules.

Measurements of the *E.M.F.* of concentration cells with silver nitrate as the dissolved electrolyte and pyridine as solvent also afford support for the view that the degree of ionisation passes through a minimum value at a particular concentration.

Transport number measurements made with silver nitrate in various solvents show that the influence of the solvent on the value of the transport ratio diminishes with falling concentration, and in dilute solution the transport numbers are almost independent of the nature of the solvent. H. M. D.

Water Correction in Conductivity Determinations. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1917, **39**, 7—24).—A theoretical paper in which the significance of the water correction in electrical conductivity determinations at very high dilutions, and the previous work on this subject are discussed. The method of deducing the exact "solvent correction," on the assumption that the water employed is in equilibrium with atmospheric carbon dioxide, has been worked out. It is shown that in the case of strong acids no correction is to be applied to the observed values throughout the ordinary range of dilutions. With acids weaker than acetic acid the correction to be applied becomes appreciable at very high dilutions. The correction in the case of exceedingly weak acids, for example, phenol, is considerable at all dilutions. In the case of bases the correction necessary is large and positive. In the case of salts of strong acids substantially accurate values are obtained by the Kohlrausch method—direct subtraction of the water conductivity. The ideal correction is slightly less than this, but only within the limits of experimental error. In the case of salts of weak acids, the true results lie between the uncorrected values and the water corrected values. The exact correction necessary varies with the

concentration of the solution and the strength of the constituent acid. Hydrogen carbonates alone require no correction. The accepted values for $\Delta\infty$ (as given by Kohlrausch) are, in the case of neutral salts, practically unaffected by the application of a carbonic acid correction to the conductivity data from which they are derived. Whether these salts follow the simple dilution law at exeedingly high dilutions is a point which cannot be satisfactorily established from the existing measurements. The confirmation of the figures of Kohlrausch, however, indicates that the equation of Kraus and Bray is applicable to neutral salts in very dilute aqueous solutions. The values of $\Delta\infty$ derived by Kohlrausch for salts of weak acids are decidedly too low—in the case of sodium fluoride by almost 1%. J. F. S.

The Measurement of Electrolytic Conductivity. II. The Telephone Receiver as an Indicating Instrument for Use with the Alternating Current Bridge. EDWARD W. WASHBURN and KARR PARKER (*J. Amer. Chem. Soc.*, 1917, **39**, 235—245). —It has been found that a properly constructed telephone receiver is greatly superior for determining the setting in an alternating current bridge to all other instruments which have been proposed for the purpose. In most cases the degree of precision attainable in the measurement is finally controlled and limited by the temperature fluctuation of the thermostat. It is calculated that a precision of one part in 10 millions may be attained by a telephone receiver with an audibility current no smaller than 10^{-9} ampere, which degree of sensitivity is obtainable with telephones of a moderate price.

The tuning of a telephone receiver to the frequency of the current employed by mechanical, electrical, and acoustical methods is discussed, together with the variation of the sensitivity with the frequency and the determination of the audibility current.

H. M. D.

New Form of Conductivity Cell for Electro-titration. HAROLD E. ROBBINS (*J. Amer. Chem. Soc.*, 1917, **39**, 646—648).—A conductivity cell is described, which allows of easy access for the burette tip, and affords a means of mixing the two liquids. The electrodes are protected in a tube which is open at the top to admit the burette. The cell is connected at the bottom by means of a double right-angle bend with a bulb which has a slightly larger capacity than the cell itself. This is used for mixing, the whole of the liquid being drawn up into the bulb and mixed by passing a few bubbles of air through it. J. F. S.

Direct Reading Ionometer. F. E. BARTELL (*J. Amer. Chem. Soc.*, 1917, **39**, 630—633).—A potentiometer is described which, used in conjunction with a calomel electrode, enables direct readings of the hydrogen ion concentrations of solutions to be made between the limits 1×10^{-0}—1×10^{-14}, that is, for solutions varying in acidity from that of a normal acid to that of a normal base.

J. F. S.

Electrical Endosmose. I. T. R. BRIGGS (*J. Physical Chem.*, 1917, **21**, 198—237).—Previous observations relative to the phenomenon of electrical endosmose are discussed with reference to the electro-osmotic behaviour of solutions, and the various theories which have been advanced to account for electrical endosmose are subjected to a critical analysis.

In the author's opinion the most satisfactory working hypothesis is that advanced by Freundlich (*Kapillarchemie*, 1909, 245) and Bancroft (A., 1912, ii, 623), according to which the sign of the charge on a diaphragm depends on the relative adsorption of cations and anions, being positive if the cations are adsorbed to a greater extent than the anions, and negative if the reverse is the case. The development of this hypothesis leads to the conclusion that any change in the character of the adsorption will exert an influence on the electro-osmotic behaviour. The direction of electro-endosmotic flow indicates the sign of the charge on the diaphragm, and the rate of flow is proportional to the intensity of the charge if the potential gradient through the diaphragm is constant. Furthermore, it is held that the electrical endosmose furnishes a measure of the tendency of a solid to form an electrical suspension in a given liquid. It bears no relation, however, to the tendency of the solid to form non-electrical suspensions, such as are produced by the adsorption of solvent, solute, or neutral colloid. H. M. D.

Two Rules on the Connexion between some Physical Properties of Homologous Series of Organic Compounds. W. HERZ (*Chem. Zeit.*, 1917, **41**, 183).—The product of the coefficient of expansion and the boiling point in absolute degrees is approximately a constant for the members of a given homologous series and does not vary much for the different series. The following mean values have been calculated for various series. Primary aliphatic alcohols, 0·0383; aliphatic monocarboxylic acids, 0·0446; aliphatic ketones, 0·0468; aliphatic ethers, 0·0487; aliphatic esters, 0·047; aliphatic *iso*-hydrocarbons, 0·0493; alkyl iodides, 0·0411; and aromatic hydrocarbons, 0·0421. The product of the specific heat at 20°, multiplied by the density at the same temperature, is approximately a constant for a given series, but varies considerably from series to series; thus for the following series the mean values are: aliphatic primary alcohols, 0·468; aliphatic hydrocarbons, 0·364; and aliphatic monocarboxylic acids, 0·557. It is noted that the specific heat continuously decreases as the series is ascended in the case of the alcohols and hydrocarbons, but in the case of the acids it alternately rises and falls. J. F. S.

The Le Chatelier-Brain Principle. LORD RAYLEIGH (T., 1917, **111**, 250—252).—In agreement with Ehrenfest (*Zeitsch. physikal. Chem.*, 1911, **77**, 2), the author considers that the principle is entirely ambiguous in its ordinary formulation, and that it is necessary to discriminate between the various parameters by which the condition of a system may be defined before the principle can be applied to yield definite results. H. M. D.

Determination of the Critical Temperatures and Pressures of Alkylamines and Alkyl Chlorides. A. BERTHOUD (*J. Chim. Phys.*, 1917, **15**, 3—29).—Using a modification of Pellaton's method (compare A., 1916, ii, 245) by means of which the critical temperature and pressure could be determined in one operation, the author has determined the values of these constants for five alkylamines and two alkyl chlorides. The results obtained and the values calculated for the constants a and b in van der Waals's equation are:

	t_c.	π (atmos.).	$10^5 . a$.	$10^6 . b$.
Methylamine	156·9°	73·6	1421	2675
Ethylamine...	183·2	55·54	2113	3754
Propylamine	223·8	46·76	2988	4865
Dimethylamine ...	164·58	52·40	2069	3826
Diethylamine	223·3	36·58	3816	6216
Ethyl chloride ..	187·2	51·72	2318	4074
Propyl chloride ...	230·05	45·18	3170	5098

These values are, in general, considerably different from those obtained by Vincent and Chappuis (compare A., 1886, 963), and with these new values the anomalies, which have been shown to exist, for the amines, in several relations in which the critical constants enter, disappear. (Compare van Laar, A., 1916, ii, 386).

In an appendix the author considers the relationship between the constant a and the molecular weight in an homologous series, and shows, by reference to several series of compounds, that this ratio may, in certain cases, reveal polymerisation at the critical point. Various data are quoted which seem to indicate that ammonia is polymerised in the liquid state and at the critical point. He suggests that the fact that the nitriles satisfy Trouton's law, although they are polymerised, may be explained on the basis that the heat of dissociation of the complex molecules is very small.

W. G.

Improvements in Calorimetric Combustion, and the Heat of Combustion of Toluene. THEODORE W. RICHARDS and HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1917, **39**, 341—354).—Improvements are described in the Berthelot calorimetric bomb in connexion with (1) the method of sealing the bomb; (2) the method of regulating and effecting the complete combustion of the substance under examination; (3) the method of igniting the substance and the automatic control of the temperature of the environment by a special synthermal regulator; and (4) the method of analysis of the residual gases for traces of unburnt carbon monoxide. The heats of combustion of naphthalene and of toluene have been determined and the following values obtained: naphthalene being taken as standard, 1 gram developed 9622 20°-calories and raised the temperature of the apparatus 3·616°; hence since 1 gram of toluene raised the temperature 3·821°, it has a heat of combustion 10,158 18°-calories, or 42·47 kilojoules per gram weighed in a vacuum.

J. F. S.

Thermal Chemistry of Pyridine. J. HOWARD MATHEWS, ELLIS L. KRAUSE, and VAN L. BOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 398—413).—The heats of solution in pyridine of silver nitrate, silver thiocyanate, mercuric chloride, and mercuric iodide, and their compounds with pyridine, have been determined, and from the values obtained the heat of pyridination has been calculated. The method adopted was a modification of that previously used by Krause. The measurements were made in a Dewar vessel containing 400 grams of pyridine. The specific heat of every solution was determined by heating the solution electrically by a known amount of current and measuring the rise of temperature. All temperature measurements were made with a Beckmann thermometer. The specific heat of pyridine at 21° was found to be 0·3907. From the experimental data the following values were obtained, in which the symbol *py* signifies 200 molecules of pyridine: (1) $AgNO_3 + py = AgNO_3py + 17{,}036$ cal.; (2) $AgNO_3,3C_5H_5N + py = AgNO_3py - 2606$ cal.; (3) $AgNO_3 + 3C_5H_5N = AgNO_3,3C_5H_5N + 19{,}636$ cal.; (4) $AgNO_3,2C_5H_5N + py = AgNO_3py + 969$ cal.; (5) $AgNO_3 + 2C_5H_5N = AgNO_3,2C_5H_5N + 16{,}067$ cal.; (6) $AgNO_3,2C_5H_5N + C_5H_5N = AgNO_3,3C_5H_5N + 3569$ cal.; (7) $AgCNS + py = AgCNSpy + 4364$ cal.; (8) $AgCNS,C_5H_5N + py = AgCNSpy + 250$ cal.; (9) $AgCNS + C_5H_5N = AgCNS,C_5H_5N + 4114$ cal.; (10) $HgCl_2 + py = HgCl_2py + 13{,}387$ cal.; (11) $HgCl_2,\frac{2}{3}C_5H_5N + py = HgCl_2py + 4974$ cal.; (12) $HgCl_2 + \frac{2}{3}C_5H_5N = HgCl_2,\frac{2}{3}C_5H_5N + 8413$ cal.; (13) $HgCl_2,C_5H_5N + py = HgCl_2py + 1932$ cal.; (14) $HgCl_2 + C_5H_5N = HgCl_2,C_5H_5N + 11{,}455$ cal.; (15) $HgCl_2,2C_5H_5N + py = HgCl_2py - 5359$ cal.; (16) $HgCl_2 + 2C_5H_5N = HgCl_2,2C_5H_5N + 18{,}746$ cal.; (17) $HgCl_2,C_5H_5N + C_5H_5N = HgCl_2,2C_5H_5N + 7291$ cal.; (18) $HgI_2 + py = HgI_2py + 9974$ cal.; (19) $HgI_2,2C_5H_5N + py = HgI_2py - 4921$ cal.; (20) $HgI_2 + 2C_5H_5N = HgI_2,2C_5H_5N + 14{,}895$ cal. J. F. S.

Surface Tension. V. Structure of the Surfaces of Liquids, and Solubility as Related to the Work done by the Attraction of Two Liquid Surfaces as they Approach each other. WILLIAM D. HARKINS, F. E. BROWN, and E. C. H. DAVIES (*J. Amer. Chem. Soc.*, 1917, **39**, 354—364. Compare A., 1916, ii, 222, 223).—The authors have determined the change of free surface energy when one square centimetre of interface is formed between two liquids. The measurements have been made between water on the one hand and a number of paraffins and the related cyclic hydrocarbons, olefines, halogen derivatives of the paraffins and benzene hydrocarbons, alcohols, acids, esters, amines, ethers, and mercaptans on the other. The temperature of the experiments varied between 10° and 40°. The data obtained indicate that at the interface between water and another liquid, the molecules in the surface of that liquid set themselves in such a way as to turn their most active or polar groups towards the surface of the water. At such surfaces, therefore, liquids show a structure. The decrease of free energy, when the surface of a second liquid approaches that of water (a polar liquid), depends primarily on the

most active or polar group present in the molecule, and in a secondary way on the shape and size of the molecule. The solubility in water is related to this decrease of free energy, which more or less perfectly measures the attraction of the active group for the water molecule. Thus the presence of a very polar group, such as the carboxyl group, the carbonyl group, cyanide group, hydroxyl group, or the amide group, is sufficient to make the molecule of an organic substance soluble in water if the polar group does not have to pull into the solution a slightly polar group which is too long or too large. Whilst slightly polar groups, such as the methyl group, are attracted by water, the attraction is much smaller than that of the polar groups. The active groups cited above, and also ether, contain either oxygen or nitrogen atoms. The sulphur atom is much less active than these, but is much more active than the methyl group. Double or triple bonds between carbon atoms act as active groups, and benzene shows a much larger value for this decrease of free energy than the corresponding six carbon atom hydrocarbons which do not contain double bonds. True solubility is a molecular scale phenomenon, and is dependent on the attractions of the different parts of the various molecules for each other, and on the shapes and sizes of the molecules which must be fitted together to make a solution. The space occupied by a molecule depends on the extent of its kinetic agitation, so that the solubility of substances is highly dependent on temperature. J. F. S.

Surface Tension. VI. Orientation of Molecules in the Surfaces of Liquids. Energy Relations at Surfaces, Solubility, Adsorption, Emulsification, Molecular Association, and the Effect of Acids and Bases on Interfacial Tension. WILLIAM D. HARKINS, EARL C. H. DAVIES, and GEORGE L. CLARK (*J. Amer. Chem. Soc.*, 1917, **39**, 541—596. Compare preceding abstract).—A continuation of the work of the previous paper (*loc. cit.*). The paper is chiefly theoretical, but a number of experiments are described on the measurement of the surface tension of sodium oleate and magnesium oleate solutions and their interfacial tensions towards benzene at 20°. It is shown that the molecules of liquids seem to be oriented, and in such a way that the least active or polar groups are oriented toward the vapour phase. The general law for surfaces is: If the structure of the surface of a liquid is supposed to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapour phase, and at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic and symmetrical, then the orientation will consist of a displacement of the electromagnetic fields of the atoms. This molecular orientation sets up what is commonly called "the double electrical layer at the surface of liquids and solids. On applying this law to a few special cases, the following orientations are deduced for several

pure liquids: In water the hydrogen atoms turn toward the vapour phase and the oxygen toward the liquid. With organic paraffin derivatives, the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, CO·OH, CO·OM, CO·OR, NH_2, $NH·CH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the interior of the liquid. If any of these organic compounds are dissolved in water, their orientation on the water surface is the same as given above, with the active groups inward. The behaviour of these various groups is tabulated in the paper. At interfaces between two pure liquids the molecules turn so that their like parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid *A* are as much like *A* as possible, and the ends toward *B* are as much like *B* as possible. So at interfaces between organic liquids and water, for example, the organic radicle sets toward the organic liquid, and the polar group toward the water.

If at an interface the transition from a liquid *A* to the liquid *B* is made by a saturated film of solute molecules, which may be termed *A*—*B*, that is, they have one end like *A* and the other like *B*, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs/cm.^{2}. If the solvent is polar, such as water, then solutes will in general be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively absorbed. Contrary to previous work, the present results show that bases do not lower markedly the interfacial tension between benzene and water. This is an important fact on account of its physiological applications. The important energy functions at surfaces are the total surface energy (μ or E_s), the free surface energy (γ), the latent heat of the surface (b), and the specific heat of the surface (c) all being for unit area. The total surface energy is independent of the temperature so long as $d\gamma/dT$ is constant, and is more characteristic of chemical constitution than the other functions. It is shown that the Eötvös–Ramsay–Shields method for the calculation of molecular association is of little value. A very extensive table of 336 liquids has been compiled in which values of E_s, γ, $d\gamma/dT$, and $(d\gamma/dT)/\gamma_0$ are given. The relationships of these data to the orientation are given in the other table already mentioned. A discussion is entered into on (i) the substitution products of the paraffins, (ii) the substitution products of benzene, and (iii) the orientation of the substitution products of benzene.

Films of solutes positively adsorbed at either liquid–vapour surfaces or liquid–liquid interfaces frequently become saturated. The rapidity with which saturation occurs depends on the nature of the solute, and increases with the length of the insoluble end of the molecule. Thus sodium oleate in water is very highly adsorbed, and the surface tension of the solution decreases with extreme rapidity. After the concentration of the solution reaches

the value $0{\cdot}002N$, the surface tension no longer decreases, but remains constant up to $0{\cdot}1N$ or more, which proves that the film has become saturated. The stability of the emulsoid particles seems to be brought about by orientation of molecules at the interface with the dispersion medium. The best emulsifying agents, for example, have very long molecules, with a polar or active group at one end of the molecule. For the emulsoid particle to be stable, the molecules which make the transition from the interior of the drop to the dispersion medium, or the molecules of the film, should fit the curvature of the drop. From this point of view the surface tension of very small drops is a function of the curvature of the surface. J. F. S.

Freezing of Water Absorbed in Lampblack. H. W. Foote and Blair Saxton (*J. Amer. Chem. Soc.*, 1917, **39**, 627—630. Compare A., 1916, ii, 230).—A continuation and confirmation of previous work. Lampblack containing absorbed water has been subjected to temperatures down to −78° in a dilatometer, and curves plotted of the temperature and dilatometer readings; heating curves were also obtained. The experiments show that the density of water which has been absorbed or adsorbed by lampblack is essentially the same as that of other water at the same temperature, although the last of the water did not freeze until the temperature was below −35°. The "apparent capillary water" in these experiments amounts to three-quarters of the weight of the carbon. The curves obtained in the present work differ only in one respect from those obtained from hydrogels. In hydrogels, the heating curves take on a decided curvature at as low a temperature as −20°, showing that the ice begins to melt at this temperature, whereas in the present case the curve is a straight line right up to zero, which shows that ice once formed, at no matter what temperature, does not melt again until the temperature is very near to zero. J. F. S.

Adsorption of Chromium Oxide by Hide Powder. A. W. Davison (*J. Physical Chem.*, 1917, **21**, 190—197).—The quantity of chromic oxide absorbed by standard hide powder has been determined in a series of experiments in which the only variable factor was the strength of the chrome tanning solution, which was made up by mixing a solution containing 120 grams of chrome alum in 1000 c.c. of water with a solution containing 30 grams of sodium carbonate in 100 c.c. of water.

Two grams of the hide powder were shaken for an hour with 250 c.c. of a solution containing 10 grams of sodium chloride per litre to ensure complete soaking of the powder. A measured volume of the tanning solution, made up to 25 c.c. by the addition of water, was then added to the flask containing the hide powder, and the shaking continued for four hours.

In order to estimate the absorbed chromic oxide, the contents of the flask were filtered, and the liquid adhering to the chromed

hide powder removed as completely as possible by centrifugal action. The powder was then acted on with a little nitric acid and the dry residue heated in an electric furnace at a dull red heat. The sodium chloride and potassium sulphate in the ignited residue were removed by washing, and the residue, after correction for the ash of the hide powder, was taken as representing the chromic oxide absorbed.

If the quantity of the chromic oxide absorbed by 2 grams of hide powder is plotted against the concentration of the chromium in the residual solution, a continuous curve is obtained, the form of which corresponds with the ordinary adsorption formula. The results are therefore considered to support the view that the initial step in the process of chrome tanning consists in the adsorption of chromic oxide. H. M. D.

Selective Adsorption and Differential Diffusion. JEROME ALEXANDER (*J. Amer. Chem. Soc.*, 1917, **39**, 84—88).—A paper in which several qualitative experiments are described to show the different rates of diffusion of substances through colloids. This is followed by a discussion on the effects of differential diffusion and selective adsorption in connexion with the action of antitoxins on toxins, and with root formation and shoot formation in plants. J. F. S.

Inconstancy of the Solubility Product. II. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1917, **39**, 218—231. Compare A., 1910, ii, 936).—Measurements have been made at 25° of the solubility of silver bromate, thallous chloride, and lead chloride in aqueous solutions containing varying amounts of acetic acid, and also of the solubility of tetramethylammonium iodide in solutions of potassium hydroxide and ammonium hydroxide. In four out of five cases the solubility decreases regularly with increasing quantity of the soluble electrolyte, but with lead chloride there is at first a slight increase followed by a very marked decrease. These results indicate that the ionic solubility product decreases with increase in the concentration of the soluble electrolyte. The proof of this is furnished by a consideration of the equilibrium in the solution which is saturated with respect to AB. As a consequence of double decomposition, the solution contains AB, CD, AD, and CB, and the four component ions. If the ion concentration is represented by capital and the concentration of the non-ionised molecules by small letters, then the total solubility, m, of AB may be expressed by $m = A + a + c$ and $m = B + a + \mathrm{d}$. Multiplying these equations and extracting the square root gives $m = \sqrt{AB} + X$, in which X has a positive value. From this, it follows that, if m becomes less than $\sqrt{AB}$, the ionic solubility product must have a value which is smaller than that for a saturated solution of AB in pure water. The data obtained in the above measurements show that this condition is attained in four out of five cases, the exception being the solution of tetramethylammonium iodide in aqueous ammonia. H. M. D.

Solubilities of Several Substances in Mixed Non-aqueous Solvents. II. J. W. MARDEN and MARY V. DOVER (*J. Amer. Chem. Soc.*, 1917, **39**, 1—7. Compare A., 1916, ii, 418).—The authors have determined the solubility at 25° of lithium chloride in mixtures of acetone and benzene, and of ethyl acetate and benzene; of mercuric chloride in mixtures of ethyl ether and chloroform, acetone and benzene, and ethyl acetate and benzene; and of salicylic acid in mixtures of acetone and benzene and ethyl acetate and benzene. Solubility determinations of the same substances at the same temperature have also been made in the pure solvents. It is shown that of the sixteen cases examined in the present and the preceding paper, five yield curves which present breaks, whilst the other eleven yield smooth solubility–composition curves. Of these eleven, in six cases the solubility was reduced by any given change in the percentage composition of the solvent by a constant fraction of the total difference between the solubility in the solution in question and in the poorer solvent. This is expressed by the equation $(C_1-C_2)/C_1=(C_2-C_3)/C_2=K$. In the five remaining cases, the relationship is expressed by the equation $(C_1-C_2)/\sqrt{C_1}=(C_2-C_3)/\sqrt{C_2}=K$. J. F. S.

The Formation of Salt Crystals from a Hot Saturated Solution. E. TATUM LONG (*Amer. J. Sci.*, 1917, [iv], **43**, 289—292).—A description of an experiment, with photographs of the apparatus used, designed to show that crystals during development exert a lateral pressure sufficient to permit continued growth even against opposing external forces. In the experiment described, a hot saturated solution of common salt, under a small hydrostatic pressure, is forced into a closed rubber tube in which crystals grow and eventually burst the rubber. E. H. R.

The Constitution of Mixed Crystals. L. VEGARD and H. SCHJELDERUP (*Physikal. Zeitsch.*, 1917, **18**, 93—96).—To decide whether mixed crystals of isomorphous substances consist simply of superimposed layers of the two components or of a more intimate interpenetration, mixed crystals of potassium chloride and potassium bromide, and of potassium and ammonium bromides, in varying proportions have been examined by means of X-rays. The reflection method of Bragg was used, and it was found that the reflection maxima from cube and dodecahedron faces in the case of the mixed crystals were always normal in character and fell between those of the two components. Were the mixed crystals formed of alternating layers of the two components, it was to be expected that double maxima would be detected corresponding with the two reflection spectra from the components.

It is concluded that in mixed crystals of, for example, potassium chloride and bromide there is a space lattice similar to that of either component, some of the halogen atoms of the one kind being replaced by those of the other kind. The molecular volumes of the components undergo modification, that of the

chloride being increased, that of the bromide diminished. If, in a 50% mixture of the two salts, the halogen atoms of the two kinds alternate regularly in the structure, it is to be expected that a new reflection maximum would be observed from the octahedron face (111) owing to the doubling of the lattice constant in the direction perpendicular to this face. Such a maximum could not, however, be detected, owing either to its necessarily feeble character or to the fact that the distribution of the halogen atoms of the two kinds is not of such a symmetrical character as to produce it. E. H. R.

X-Ray Analysis and Topic Axes of the Alkali Sulphates and their Bearing on the Theory of Valency Volumes. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 72—89).—This paper is devoted to an attack on the Barlow-Pope theory of the relation between atomic volume and valency in crystals. The isomorphism of ammonium salts with corresponding salts of the alkali metals potassium, rubidium, and cæsium is discussed, in particular the close approach to equality between the structural dimensions of crystals of corresponding ammonium and rubidium salts. On account of their similar molecular volumes, isomorphous ammonium and rubidium salts readily form mixed crystals. Crystals of the sulphates have now been subjected to *X*-ray examination by Ogg and Hopwood (compare *Phil. Mag.*, 1916, [vi], **32**, 518), and the results fully confirm the close structural similarity of the ammonium and rubidium salts. The structural unit of the rhombic crystal contains in each case 4 molecules, as had been previously suggested by the author. The structures of these salts are held to be inconsistent with the valency volume theory, which gives to $(NH_4)_2SO_4$ a volume$=24$ and to Rb_2SO_4 a volume$=12$, whereas the actual volumes of the space units of the crystals are very nearly equal. E. H. R.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. I. General Colloido-chemical Investigation of Salep Extract. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 83—101. Compare this vol., ii, 168, 169).—An account is given of the preparation of colloidal extracts of tubera salep and of observations on the stability of these colloidal solutions, with special reference to the influence of concentration, temperature, and added electrolytes.

The data obtained in measurements of the viscosity of solutions of varying concentration are discussed in reference to Hatschek's theory that water is adsorbed by the colloidal particles, and it is calculated that 1 gram of the colloid combines with about 27 grams of water. In an electric field the colloidal particles move towards the cathode.

Observations made with dialysed and undialysed extract show considerable differences in regard to the influence of the several factors which have been examined. H. M. D.

Antagonistic Electrolytes and Jelly Formation. G. H. A. CLOWES (*Proc. Amer. Soc. Biol. Chem.*, 1916, viii—ix; *J. Biol. Chem.*, 1917, **29**. Compare A., 1916, i, 583).—When sodium chloride is added in increasing proportion to aqueous suspensions of soaps or lipoids, the dispersion of the particles in water is at first promoted and reaches an optimum at approximately $0{\cdot}15M$-sodium chloride, which corresponds closely with the concentration of this substance in the blood. Subsequently, an aggregating effect is exerted, precipitation occurring at a concentration of $0{\cdot}35$ to $0{\cdot}4M$-sodium chloride, which appears to be the limiting concentration for the maintenance of life of marine organisms, of mice on intravenous injection, and the precipitation point for emulsions, jellies, and a variety of other physical systems.

Koch's curve (A., 1907, i, 573) showing the amount of calcium chloride required to precipitate lecithin at different concentrations of sodium chloride corresponds closely with curves obtained by the drop method (Clowes, *loc. cit.*) when sodium chloride is added in increasing proportion to an aqueous phase containing a constant amount of soap passed through neutral oil. The similarity in these antagonistic curves of calcium chloride and sodium chloride and other salts having a more readily adsorbed anion in such widely diversified systems as living protoplasm, the blood-clot emulsions, soap jellies and films, and soap and lipoid suspensions, and the existence of the common limiting concentrations at which individual salts like sodium chloride and calcium chloride produce inhibiting effects in all these systems, suggest the probability that protoplasmic equilibrium and the formation of reversible protoplasmic jellies are dependent on what the author designates as an imperfect reversal of phase relations promoted by the action of antagonistic electrolytes on interfacial films of soap and lipoid, just as in reversal of equilibrium in the case of emulsions of oil and water. H. W. B.

Plasticity. EMIL PODSZUS (*Kolloid Zeitsch.*, 1917, **20**, 65—73).—A discussion of the factors which determine the plasticity which is characteristic of mixtures of clay and water in their application in the ceramic industries. The author adopts the view that the coagulation of substances in sol form is an essential feature of such systems, and it is shown that many substances, other than clays, may be transformed into sols with plastic qualities which are quite similar to those familiarly associated with the clays. H. M. D.

The Laws of Swelling. I. The Swelling in Water without Complications. J. R. KATZ (*Koll. Chem. Beiheft*, 1917, **9**, 1—182).—The phenomena associated with the swelling of substances in contact with water have been subjected to examination in experiments with a number of different substances, in the choice of which the principal consideration was the avoidance of all possible disturbing factors. The conditions requisite for the attainment of this end are satisfied only by definite chemical compounds

which are non-porous, do not combine with the absorbed liquid, and are characterised by the absence of irreversible changes. These conditions are fulfilled by amorphous and crystalline substances, and both types have been examined.

The observations indicate the nature of the dependence of the vapour pressure, the heat of swelling, the change in volume, and the specific heat on the degree of swelling, defined as the ratio between the weight of the absorbed water and that of the dry substance under examination. The results for different substances show that the chemical nature of the substance is without influence on the general character of the phenomena associated with the swelling process.

For all the amorphous substances examined, the curve showing the relation between the vapour pressure (expressed in terms of that of pure water at the same temperature) and the degree of swelling (i) is of the same type. For small values of i, the curve runs nearly horizontal; the curve then rises, being at first convex and later concave towards the i axis, the last portion being again nearly horizontal.

The heat developed in the absorption of i grams of water by 1 gram of the dry substance is satisfactorily represented by the formula $W = Ai/(B+i)$, in which A and B are constants characteristic of the swelling substance. The corresponding contraction in volume may be expressed by a formula of the same type. These two quantities are, in fact, approximately proportional, and the ratio for different substances is of the same order of magnitude.

The decrease in the free energy and the heat development associated with the swelling process are approximately equal, and from this it follows that nearly the whole of the energy of swelling may be transformed into external work.

In the case of crystalline substances, the only measurements made were those relating to the vapour pressure. These show that the dependence of the relative vapour pressure on the degree of swelling is essentially the same as for amorphous substances.

Not only do the most various substances behave similarly in regard to the swelling processes, but it is further shown that there is a close resemblance in the relative vapour pressure, the heat of swelling, and the volume curves for mixtures of non-volatile liquids, such as sulphuric acid, phosphoric acid, and glycerol, with water. The ratio of the heat development to the volume contraction is of the same order for both groups.

This close similarity in the phenomena associated with the swelling of substances in water and in the changes which accompany the formation of binary liquid mixtures leads to the conclusion that the swelling process is to be regarded as the formation of a solid solution of water in the swelling substance. This idea is obviously incompatible with the micellary hypothesis put forward by Nägeli to explain the behaviour of swelling substances. It disposes of the necessity for the assumption of complex structural units and replaces these by the simpler molecules. The systems which result

from the swelling of substances when brought into contact with suitable liquids are accordingly to be looked on as ideal concentrated solutions. H. M. D.

Non-, Uni-, and Bi-variant Equilibria. XIII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 867—880. Compare this vol., ii, 169, 195).—A further theoretical discussion of the equilibrium relations in ternary systems with two indifferent phases. H. M. D.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. III. The Interaction of Mixed Salt Solutions and Liquid Amalgams. A Study of the Ionisation Relations of Sodium and Potassium Chlorides and Sulphates in Mixtures. G. McP. Smith and T. R. Ball (*J. Amer. Chem. Soc.*, 1917, **39**, 179—218. Compare A., 1913, ii, 124).—The behaviour of solutions containing sodium and potassium salts towards sodium potassium amalgams has been examined with a view to the elucidation of the ionisation of salts in mixtures. The equilibrium in this system corresponds with $KHg_m + Na^{\cdot} \rightleftharpoons NaHg_n + K^{\cdot}$, and by application of the law of mass action, the relation

$$[KHg_m][Na^{\cdot}]/[NaHg_n][K^{\cdot}] = C_0$$

is obtained, in which C_0 represents the constant for infinite dilution. For solutions in which the ionisation is incomplete, the equilibrium constant may be written

$$[KHg_m][NaX]_c/[NaHg_n][KX]_c = C_c,$$

where the suffix c refers to the total salt concentration. By investigation of the connexion between the value of C_c for the salt concentration c and the value C_0 corresponding with complete ionisation, it is possible to obtain information relating to the ionisation of sodium and potassium salts in their mixtures.

According to experiments with equivalent mixtures of sodium and potassium chlorides up to $4 \cdot 0N$-concentration, the value of C_c at 25° decreases linearly with increasing concentration of the solution. For equivalent mixtures of sodium and potassium sulphates at concentrations varying from $0 \cdot 2$ to $2N$, the value of C_c is nearly independent of the total salt concentration. The data for equivalent mixtures of sodium sulphate and potassium chloride up to a concentration of $3 \cdot 0N$ show, on the other hand, that C_c decreases with increasing concentration, but the decrease is not linear. The results obtained with equivalent mixtures of sodium and potassium chlorides at temperatures between 15° and 30° show that C_c decreases with rising temperature. From these results it has been possible to derive the heat change accompanying the reaction $KHg_m + NaCl = NaHg_n + KCl + (m-n)Hg$, the value found being -3000 cal.

The interpretation of the results leads to the view that complex molecules, $NaKCl_2$, are formed in the chloride solutions, and the mixed sulphate, $NaKSO_4$, in the sulphate solutions. H. M. D.

The Course of Crystallisation in Ternary Systems of Chlorides of Univalent and Bivalent Metals. TH. LIEBISCH (*Zeitsch. anorg. Chem.*, 1917, **99**, 50—66).—The ten ternary systems of chlorides of univalent and bivalent metals which have so far been investigated are theoretically reviewed, with special reference to the case in which the crystalline phases include the components *A*, *B*, and *C*, and also a binary compound with incongruent melting point, the method used being that of constructing a crystallisation path on the projection of the liquidus surface.

C. H. D.

Normal and Acid Sodium Sulphates. PAUL PASCAL (*Compt. rend.*, 1917, **164**, 628—630).—A study of the equilibrium of the ternary system H_2SO_4–Na_2SO_4–H_2O between the temperature limits $-45°$ and 210°. The results are set out as a trilinear projection of the isotherms of the surface of equilibrium of the solid and liquid phases. The diagram, coupled with a study of the cooling of the ternary mixtures, indicates that with the acid sulphates, from the manufacture of nitric acid, where the acidity is above 40·81%, solidification occurs below 184°, giving at first crystals of sodium hydrogen sulphate, until at 105° the remaining liquid solidifies to the acid salt, $NaHSO_4,H_2SO_4$. Solutions of sodium hydrogen sulphate, about 75% in strength, saturated at about 100°, give after crystallisation a residual liquid containing about 45% of sulphuric acid and only about 10% of the normal sulphate.

W. G.

A Chemical Method of Determining the Strength of Sparingly Soluble Inorganic Bases. K. A. VESTERBERG (*Zeitsch. anorg. Chem.*, 1917, **99**, 11—21).—The strength of sparingly soluble inorganic bases has usually been determined by measuring the hydrolysis of the sulphates, nitrates, or chlorides. The numbers differ very little for different bases, and better results are obtained by using the acetates and measuring the hydrolysis by the extraction method. The error caused by the disturbance of the equilibrium by removal of acetic acid by the solvent is overcome by agitating the ether solution with successive fresh quantities of the aqueous acetate solution. After three to five extractions, the ether solution is in equilibrium with unaltered acetate solution.

The ethyl ether is freed from the acid usually present in commercial samples by keeping over concentrated sodium hydroxide solution and washing with water, free from carbon dioxide, just before use. The acetate solutions are prepared from purified salts or by the addition of pure sodium acetate to the solution of the sulphate, the concentration being made 9 to 10% greater than is required to allow for the increase of volume on shaking with ether. Water free from carbon dioxide must be used. The titrations are mostly performed with 0·025*N*-barium hydroxide, with phenolphthalein as indicator. The metal in the aqueous solution must be estimated after the extraction.

C. H. D.

Propagation of Flame in Mixtures of Acetone and Air. RICHARD VERNON WHEELER and ARNOLD WHITAKER (T., 1917, **111**, 267—272).—This paper gives the results of the first of a series of investigations designed to throw light on the conditions under which the vapours of inflammable liquids used in industry form dangerously explosive mixtures with air.

The higher and lower limits of inflammability have been determined for horizontal, downward, and upward propagation of flame in tubes 2·5, 5, and 10 cm. diameter. Above 5 c.c. the diameter of the tube has little influence on the limits, and the results indicate that for large pipes the lower and upper limiting mixtures correspond respectively with about 2 and 10% of acetone vapour.

The graph obtained by plotting the speed of propagation of flame ("uniform movement") in a 2·5 cm. tube against the percentage of acetone vapour shows that the speed has its maximum value for a mixture containing 5·5% acetone. This speed is about 96 cm. per sec., and for pipes of 30, 60, and 90 cm. diameter may be expected to be respectively 2·5, 3, and 3·5 times as great.

H. M. D.

Chemical Reactions in Anisotropic Liquids. III. THE. SVEDBERG (*Kolloid Zeitsch.*, 1917, **20**, 73—76).—According to previous observations (A., 1916, ii, 306, 383), the rate of change with time of the electrical conductivity of a solution of picric acid in *p*-azoxyphenetole increases with the temperature, and changes abruptly at the clearing point of the solvent. Further experiments show that a similar effect is obtained when the anisotropy is destroyed by the addition of foreign substances, such as diphenyl and naphthalene.

The fact that the initial rate of increase of the conductivity of pure *p*-azoxyphenetole is very nearly the same as that of a solution of picric acid in this solvent, leads to the conclusion that the increase in conducting power is to be attributed to decomposition of the *p*-azoxyphenetole, and not, as previously supposed, to the decomposition of the picric acid. H. M. D.

Decomposition of Chloro- and Bromo-acetic Acids in Alcoholic Solution. HENRY W. CASSEL (*Zeitsch. physikal. Chem.*, 1917, **92**, 113—126).—The investigation of the rate of hydrolysis of chloro- and bromo-acetic acids in aqueous alcoholic solutions at 70° has shown that the velocity of the reaction diminishes in proportion to the alcohol content of the solvent. The reaction proceeds in accordance with the equation for a unimolecular change.

When the reaction mixture contained in a quartz vessel is exposed to the light emitted by an arc lamp, the reaction proceeds differently, in that acetaldehyde is produced in accordance with the equation $CH_2X{\cdot}CO_2H + C_2H_5{\cdot}OH = CH_3{\cdot}CO_2H + CH_3{\cdot}COH + HX$, in which X represents chlorine or bromine. Experiments at 18° in which the influence of the alcohol concentration was examined, show that in the case of bromoacetic acid the velocity of the reaction increases considerably with the proportion of alcohol in

the solvent, attains a maximum in 50% solution, and decreases when the alcohol content is further increased. The changes in the velocity are much smaller in the case of chloroacetic acid, and the velocity remains the same when the alcohol concentration increases from 50 to 100%. Under comparable conditions as regards the solvent, bromoacetic acid is decomposed more rapidly than chloroacetic acid, whether the reaction takes place in the dark or under the influence of light. The active rays are of wave-length less than 250 $\mu\mu$. H. M. D.

Consecutive Reactions. II. Kinetics of the Hydrolysis of the Methyl Esters of Oxalic Acid. ANTON SKRABAL (*Monatsh.*, 1917, **38**, 29—52. Compare A., 1916, ii, 477).—The rate of hydrolysis of methyl oxalate and of potassium methyl oxalate, both by acid and alkali, has been determined for a series of concentrations at 25°. The hydrolysis of the normal ester takes place in two stages, which have such different velocities that the calculation of the velocities by the method used for single-stage reactions can be effected. In alkali hydroxide solutions the rate of hydrolysis of the ester acid is still measurable, whilst that of the normal ester to the first stage is unmeasurably fast. The measurements were therefore carried out with a mixture of ammonia and ammonium chloride, the alkalinity of which is of about the same dimensions as the esters. The ratio of the velocity constants was found to be of the order 10,000 : 1. In the case of acid hydrolysis, the velocity was of the normal order and the measurements were carried out in the usual way with hydrochloric acid. In this case the ratio of the velocity constants is 2 : 1. The actual constants obtained are: first stage—alkaline hydrolysis, $k_1 = 10^6$; acid hydrolysis, $k_1 = 0{\cdot}0116$; second stage—alkaline hydrolysis, $k_2 = 10^2$; acid hydrolysis, $k_2 = 0{\cdot}0058$. J. F. S.

Reactions with Halogen-substituted Acids. II. Action of Sodium Methoxide on Monobromosuccinic Acid, α-Bromo*iso*butyric Acid, β-Bromobutyric Acid, and α-Bromopropionic Acid. E. HÖST MADSEN (*Zeitsch. physikal. Chem.*, 1917, **92**, 98—112. Compare A., 1914, ii, 260).—The interaction between sodium methoxide and the sodium salts of various halogen-substituted acids in methyl-alcoholic solution has been examined by measurements of the alkalinity and the bromide concentration after various intervals of time.

The results indicate that intermediate products are formed in the case of bromosuccinic and β-bromobutyric acids, in that the increase in the bromide concentration takes place more rapidly than the decrease in the alkali titre. These intermediate substances appear to be formed at the same rate in anhydrous methyl alcohol and in methyl alcohol which contains three gram-molecules of water per litre, but the rate of decomposition of the intermediate compounds is greater in presence of water. The formation of intermediate products appears to be characteristic of the β-substituted acids, for the experiments with α-substituted acids gave no evidence of this phenomenon.

The kinetic data are discussed in reference to the order of the several reactions investigated. H. M. D.

Reactions of both the Ions and the Molecules of Acids, Bases, and Salts. The Inversion of Menthone by Sodium, Potassium, and Lithium Ethoxides. W. A. Gruse and S. F. Acree (*J. Amer. Chem. Soc.*, 1917, **39**, 376—388).—The authors have measured the velocity of inversion of *l*-menthone in absolute alcohol solution by the ethoxides of sodium, potassium, and lithium. The measurements were carried out in 70 cm. polarimeter tubes by means of a Schmidt and Haensch polarimeter, capable of reading to 1/1000°. The rotation measurements were made with the mercury-green line 546·1, obtained from a mercury vapour lamp, using a mercury-green line Wratten filter. The reactions took place in a thermostat at 25°, which did not vary more than 0·005°. Dilute solutions varying from $N/32$ to $N/512$ were used. By substituting the molecular velocity constants K_N and the corresponding α values in the proper equations, values have been obtained for the catalytic activity of the ethoxide ion and the non-ionised molecule of the metallic ethoxide. The constants expressing the activity of the ethoxide ion have been found to be the same, whether the experiment be made with sodium, potassium, or lithium ethoxide, namely, $K_i=0{\cdot}501$, $K_i=0{\cdot}501$, and $K_i=0{\cdot}496$ respectively. The constants K_m, expressing the activity of the non-ionised molecule of the metallic ethoxide, have been found to be very close for sodium and potassium ethoxides, namely, $K_m=0{\cdot}693$ and 0·701 respectively, but somewhat smaller for lithium ethoxide, $K_m=0{\cdot}478$, which is practically the same as that found for the ethoxide ion, $K_i=0{\cdot}496$ in the case of lithium ethoxide. Making use of the above considerations, satisfactory explanations have been offered for the approximate equality of the velocity constants, K_N, found for sodium and potassium ethoxides, as well as for the deviation of the lithium ethoxide from this value; for the fact that the molecular velocity constant, K_N, for lithium ethoxide remains unchanged with dilution, whilst the same values for sodium and potassium ethoxides decrease considerably as the concentration decreases, and for the nearly identical value assumed by the velocity constants for all three ethoxides in very dilute solutions. The average values of the constants for the ionic and molecular activities have been substituted in the equation

$$K_N=K_i\alpha+K_m(1-\alpha),$$

and the calculated values of K_N have been compared with the experimental values. The average deviation is about 1·5%.

J. F. S.

Kinetics of Furfuraldehyde Formation from Pentoses (Arabinose). Robert Kremann and Hermann Klein (*Monatsh.*, 1917, **38**, 63—75).—The authors have studied the kinetics of the formation of furfuraldehyde from arabinose by the action of sulphuric acid and hydrochloric acid. Five c.c. of 1·054N-arabinose solution were mixed with 10 c.c. of 4·7N-sulphuric acid, 2·35N-sul-

phuric acid, $0{\cdot}470N$-sulphuric acid, and $4{\cdot}43N$-hydrochloric acid respectively. The flasks containing the various mixtures were sealed and heated in a thermostat at 95° for measured times. They were then withdrawn, allowed to cool for fifteen minutes, and opened. The contents were neutralised with sodium hydroxide and the furfuraldehyde distilled off, converted into furfuraldehyde semioxamazide, and weighed as such. The results are expressed in dx/dt curves, where dx represents the amount of furfuraldehyde semioxamazide formed at the time dt. The results fall on to two different curves, the one being an S-shaped curve, the other a slowly rising curve. There is no apparent reason why the results should fall on one curve rather than on the other. The author concludes that at 95° a high concentration of hydrogen ions can produce in arabinose solutions, in the course of the reaction, either a positive catalyst A, which accelerates the furfuraldehyde formation autocatalytically, or a catalyst B, which accelerates the subsidiary reaction, so that in the latter case only one-third of the quantity of the furfuraldehyde expected appears to be formed. With decreasing acid concentration the two curves come closer together, and eventually coincide to represent a reaction of the first order. The S-shaped curve is represented by the equation $dx/dt=(k_1+k_2x)(a-x)$, that is, by the typical equation for an auto-catalytic reaction. J. F. S.

Kinetics of Invertase Action. J. M. NELSON and W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1917, **39**, 790—811).—A comprehensive study of the kinetics of invertase action, the data obtained showing that (1) the velocity of inversion is directly proportional to the concentration of the invertase, (2) that the velocity is nearly independent of the concentration of the sucrose in the more concentrated sugar solutions, whilst in very dilute solutions the velocity increases with the increase in concentration of the sugar up to a maximum, (3) the velocity-coefficient increases as the inversion proceeds, (4) the results agree with the heterogeneous reaction view (compare Henri, A., 1906, ii, 13; Nelson and Griffin, A., 1916, i, 516), and contradict the view that the kinetics of invertase action conform to the unimolecular law for homogeneous reactions (compare Hudson, A., 1908, i, 605, 856). Adsorption appears to be one of the controlling factors in the kinetics of invertase action, and the curve for the velocity of inversion, the concentrations of the sucrose being taken as abscissæ, has the same general shape as adsorption curves (compare Henri, *loc. cit.*). The inversion is of a type similar to, but more complicated than, the heterogeneous catalytic reaction of the dissociation of stibine into antimony and hydrogen in the presence of antimony (compare Stock and Bodenstein, A., 1907, ii, 181). A peculiar phenomenon with regard to the dilution of invertase solution was noticed, namely, that invertase solutions could be diluted in the presence of a small amount of acid without changing their relative activity, but, if the acid was omitted, solutions of widely differing activity were obtained. W. G.

The Catalytic Influence of Acids in Lactone Formation. I. Valerolactone. HUGH STOTT TAYLOR and HAROLD WILBERFORCE CLOSE (*J. Amer. Chem. Soc.*, 1917, **39**, 422—435. Compare Henry, A., 1892, 1303).—A study of the catalytic action of hydrochloric acid and chloroacetic acid on the conversion of γ-hydroxyvaleric acid into valerolactone. The acid was prepared from the lactone as required either by the action of barium hydroxide, the barium being subsequently precipitated with the calculated quantity of $N/4$-sulphuric acid, or by the action of a suspension of lead hydroxide, the lead being afterwards precipitated with hydrogen sulphide. The values obtained with the acid prepared by the second method were consistently higher by about 3% than with the acid prepared by the first method, and at present this discrepancy cannot be explained. The conversion took place at 25° in the presence of varying concentrations of hydrochloric or chloroacetic acid, in the presence or absence of varying concentrations of the corresponding potassium salt. In the case of hydrochloric acid it is shown that the catalytic influence is not strictly proportional to the hydrogen-ion concentration as determined by conductivity measurements. The presence of potassium chloride increases the catalytic effect of hydrochloric acid. The catalytic effect can be expressed in terms of a catalytic activity of hydrogen-ion and undissociated molecule, but the ratio of these two effects is different if calculated from a series of acid concentrations or from a series of constant acid and varying neutral salt concentrations (compare Dawson and Reiman, T., 1915, **107**, 1426). The catalytic ratio in the case of hydrochloric acid is of the same magnitude as that observed in ester catalysis (compare Taylor, A., 1915, ii, 248).

The results obtained with chloroacetic acid as a catalyst show certain abnormalities, which cannot at present be satisfactorily explained. No concordant figures could be obtained from any pair of results for the catalytic ratio. W. G.

Numerical Relation of Atomic Weights to Atomic Numbers. REGINALD GRAHAM DURRANT (*J. Amer. Chem. Soc.*, 1917, **39**, 621—626).—A theoretical paper in which the author discusses the work of Harkins and Wilson on the relationships existing between the atomic weights and atomic numbers of the elements (see Harkins and Wilson, A., 1915, ii, 544). Harkins and Wilson find that the relationship between atomic weight and atomic number is given, for the lighter elements, by the equation $W = 2n + \{\frac{1}{2} + [(-1)^{n-1} \times \frac{1}{2}]\}$, but for the heavier elements another term has to be introduced, and the equation becomes

$$W = 2(n + n') + [\tfrac{1}{2} + \tfrac{1}{2}(-1)^{n-1}].$$

The n' values are not given by the above-mentioned authors, and a table of these values is appended to the present paper. A graph of the n' values against the atomic numbers approximates on the whole to four straight lines: (1) a horizontal line along the axis from helium to chlorine; (2) a shorter horizontal line from titanium to cobalt ($n' = 2$); (3) a long line from copper to bismuth inclined at an angle the tangent of which is $\frac{1}{3}$; and (4) a

short line parallel to (3), but above it, from niton to uranium. The slope in the curves (3) and (4) can be reduced to the horizontal by obtaining the values $2[n+(n-29)/3]$; this is done in the paper, and the values $(W-2n)$ and $\{W-2[n+(n-29)/3]\}$ have been plotted against the atomic numbers. The deviations of the atomic weights from the doubled atomic numbers are considered.

J. F. S.

Twenty-fourth Annual Report of the Committee on Atomic Weights. Determinations Published During 1916. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1917, **39**, 333—341).—A *résumé* of the atomic weight determinations of the year 1916, which includes the numerical details of determinations on hydrogen (Burt and Edgar, A., 1916, ii, 427), H=1·00769; argon (Schultze, A., 1915, ii, 833), A=39·945; zinc (Baxter and Grose, A., 1916, ii, 327), Zn=65·381; bromine (Moles, A., 1916, ii, 526), Br=79·926; yttrium (Hopkins and Balke, this vol., ii, 34), Yt=88·91; columbium (Smith and van Haagen, A., 1915, ii, 692), Cb=93·13; cadmium (Baxter, Grose, and Hartmann, A., 1916, ii, 327), Cd=112·407; tin (Baxter and Starkweather, A., 1916, ii, 637), Sn=118·703; neodymium (Baxter, Whitcomb, Stewart, and Chapin, A., 1916, ii, 325), Nd=144·261; dysprosium (Engle and Balke, this vol., ii, 259), Dy=164·228; radioactive lead (Richards and Wadsworth, this vol., ii, 91), Pb(Ra)=207·183—206·084; lead (Œchsner de Coninck and Gérard, this vol., ii, 33), Pb=206·98; bismuth (Œchsner de Coninck and Gérard, A., 1916, ii, 189), Bi=208·50.

J. F. S.

The Structure of Inorganic Compounds. SAMUEL HENRY CLIFFORD BRIGGS (T., 1917, **111**, 253—267).—The author has previously attempted (T., 1908, **93**, 1564) to devise formulæ for complex salts on the basis of the conception of duplex affinity, and a further study of this hypothesis has now been made from the point of view of the electron theory.

In addition to the distinction between positive and negative affinity, a further distinction is made between primary and secondary affinity. The secondary affinity only shows itself when the primary affinity has come into play. This is illustrated by reference to the ammoniacal copper compounds. The examination of these shows that cuprous compounds combine with a maximum of three molecules of ammonia and cupric compounds with six molecules, whilst metallic copper, that is to say, the neutral atom, is incapable of direct combination with ammonia. It would seem, therefore, that the copper atom develops negative (secondary) affinity when it has lost an electron, and when it has lost two electrons the negative affinity becomes more pronounced. Combination of atoms as a result of the saturation of primary affinity only is accompanied by a transfer of electrons from one atom to the other, whereas no such transfer takes place when the secondary affinities are saturated.

The theory is examined in reference to the constitution of ammonia and ammonium salts, the strengths of acids and bases, the stability of the compounds of ammonia with metallic salts, and the phenomenon of polymerisation. This leads to the view that compounds formed by the saturation of primary affinity only are of the "strong electrolyte" type, those formed by the saturation of secondary affinity only of the "molecular compound" type, and those formed by the saturation of both kinds of affinity of the "organic compound" or "paraffin" type. These three categories represent only extreme types, and most compounds are of intermediate character.

It is pointed out that the formulæ suggested on the above theory are purely affinity, and not valency formulæ. It may, indeed, be doubted whether a theory of valency is admissible in modern inorganic chemistry. H. M. D.

A Simple Gas Generator. R. O. FERNANDEZ (*J. Amer. Chem. Soc.*, 1917, **39**, 271).—A generator of the Kipp type constructed from apparatus available in every laboratory. H. M. D.

An Efficient Desiccator. L. S. PRATT (*J. Amer. Chem. Soc.*, 1917, **39**, 271—272).—The apparatus consists of a Buchner funnel connected below through a stopcock and safety flask with a water-pump. Resting on the funnel is a heavy brass disk with a ring or sheet of rubber cemented on the lower surface, which affords an airtight joint when pressure is brought to bear on the disk by means of screws acting between the disk and a metal collar beneath the funnel. A brass tube passes through the centre of the disk, and this tube is connected through a stopcock to a system of drying towers. The material to be dried is placed in the funnel, the disk placed in position, and by means of the pump a current of dry air or inert gas is forced through the funnel. If the material requires to be dried at an elevated temperature, the apparatus may be enclosed in an air-bath. H. M. D.

Laboratory Experiment. Enrichment of Illuminating Gas. ROSS ALLEN BAKER (*J. Amer. Chem. Soc.*, 1917, **39**, 646).—A trap, consisting of a wide-mouthed bottle, is introduced between the gas outlet and a Bunsen burner. A copper wire is bound round one of the tubes which project through the stopper and serves to support a piece of calcium carbide. The Bunsen is lighted so that it is quite non-luminous, the carbide is then shaken into water, contained in the bottle, when the flame becomes luminous owing to the liberated acetylene. J. F. S.

Inorganic Chemistry.

Electrolytic Formation of Perchlorate. E. L. MACK (*J. Physical Chem.*, 1917, **21**, 238—264).—The mechanism of the formation of perchlorate by the electrolysis of chlorate solutions is usually regarded as that expressed by the equation $2ClO_3' + H_2O + 2F = HClO_4 + HClO_3$, a view first put forward by Oechsli (A., 1904, ii, 22). It is pointed out that this theory rests on several assumptions for which there is no experimental evidence, and that it does not account satisfactorily for the very marked decrease in the yield of perchlorate when platinised platinum anodes are substituted for smooth platinum anodes nor for the decrease in the efficiency with rising temperature. On the other hand, it is claimed that the phenomena associated with the electrolytic formation of perchlorate can be easily and satisfactorily explained on the assumption that the action consists in the combination of the chlorate ions with active oxygen resulting from the discharge of oxygen or hydroxyl ions at the anode. This view is supported by Schoch's experiments (A., 1911, ii, 14), which showed that in a $N/3$-solution of potassium chlorate with an iron anode, perchlorate formation begins when the anode potential reaches $+0{\cdot}023$ volt, whereas oxygen is not evolved until the anode potential reaches $+1{\cdot}5$ volts. It is thus clear that the electrolytic formation of perchlorate absorbs an amount of energy which is very much smaller than that required for the liberation of oxygen or the discharge of the chlorate ion.

In support of the author's theory, it has been found that chlorate may be oxidised to perchlorate by persulphuric acid, ozone, or hydrogen peroxide in acid solution. The oxidation may also be effected by the action of oxygen which has been activated by ultraviolet light. The reaction may be represented by the equation $HClO_3 + O = HClO_4$, and for a given concentration of chlorate the rate of oxidation will depend on the concentration of the active oxygen. The conditions obtaining in the experiments in which the chlorate has been oxidised to perchlorate by purely chemical agents are quite comparable with those attending electrolysis, and there are thus grounds for the assumption that the action is of the same kind. H. M. D.

Preparation of Sulphurous Acid. EDWARD HART (*J. Amer. Chem. Soc.*, 1917, **39**, 376).—Fuming sulphuric acid containing 30% SO_3 is warmed with lump sulphur. The sulphur dissolves, forming a blue solution, from which, on warming, sulphur dioxide is given off mixed with some sulphur trioxide. Evolution of sulphur dioxide ceases when all the sulphur trioxide has been acted on and the sulphur melts. W. G.

The Synthesis of Ammonia. HENRY LE CHATELIER (*Compt. rend.*, 1917, **164**, 588—590).—Historical. The author claims priority over Haber for the synthesis of ammonia under pressure.
W. G.

The New Values of the Atomic Weights of Carbon and Sulphur in the International Table for 1916. E. MOLES (*J. Chim. Phys.*, 1917, **15**, 51—59).—Further evidence is brought in support of Guye's view (compare this vol., ii, 198) that the revisions of the atomic weights of carbon and sulphur proposed for 1916 by the International Committee are premature and not justified. Recalculating the values from the results of Richards and Hoover (compare A., 1915, ii, 96), based on the atomic weight of sodium, the author arrives at the results C = 11·996—12·001 and S = 32·048—32·056.
W. G.

The Faulty Values of the Atomic Weights of Carbon and Sulphur. PH. A. GUYE (*J. Chim. Phys.*, 1917, **15**, 60—63).—Further arguments in support of Moles's views (compare preceding abstract).
W. G.

Crystallographic Constants of some Artificial Crystals. HERM. ROSE (*Centr. Min.*, 1917, 85—87).—Cæsium dithionate, $Cs_2S_2O_6$, crystallises in the trapezohedral tetartohedral class of the hexagonal system [$a:c = 1:0·6316$]. It is isomorphous with potassium and rubidium dithionates, the angular measurements being very close to those of the latter. Optically, the crystals are positively uniaxial and circularly polarising. For yellow light, $\omega = 1·444$, $\epsilon = 1·491$.

The hydrated salt, $2Cs_2S_2O_6,H_2O$, crystallises in the holohedral class of the rhombic system [$a:b:c = 0·8832:1:0·5058$]. The optic axial plane is (010), the acute positive bisectrix $\perp$(010), $2E_{Na} = 51·5°$, $v > \rho$. Measurable crystals of the corresponding rubidium salt were not obtained.

Terpin, $C_{10}H_{18}(OH)_2$, is rhombic holohedral [$a:b:c = 0·7888:1:0·8224$]. There is a perfect cleavage parallel to (001). The optic axial plane is also parallel to (001), the axial angle in monobromonaphthalene for the green mercury line $\lambda = 546·1\ \mu\mu$ being $2H = 72°5'$. For the same line, $\alpha = 1·5209$, $\beta = 1·5292$, $\gamma = 1·5416$, whence $2V = 79°0'$. Calculated from $2H$ and β, $2V = 79°42'$.
E. H. R.

The Oxy-salts of the Alkaline Earth Metal Haloids. Equilibria in Ternary Systems. I. J. MILIKAN (*Zeitsch. physikal. Chem.*, 1917, **92**, 59—80).—The basic salts formed by the alkaline earth metal haloids have been derived from a study of the equilibrium relations in the ternary system formed by the alkaline earth metal haloid, the corresponding hydroxide and water. The results obtained with calcium chloride and bromide and with

barium chloride, bromide, and iodide have been previously described (A., 1912, ii, 760).

The data for calcium iodide at 25° show the existence of the basic salt, $CaI_2,3CaO,16H_2O$, which is stable in contact with solutions containing from 28·44 to 66·68% of calcium iodide. The only basic chloride of strontium has the composition $SrCl_2,SrO,9H_2O$, and this only exists in contact with solution at temperatures above 20·5°. Below this temperature the chloride, $SrCl_2,6H_2O$, and the hydroxide, $SrO,9H_2O$, may co-exist as solid phases in contact with aqueous solutions. The solution saturated with respect to these substances at 0° contains 0·31% of strontium oxide and 30·58% of strontium chloride.

Observations at 25° show that strontium bromide forms the basic salt $SrBr_2,SrO,9H_2O$. At this temperature it can only exist in contact with solutions containing from 40·66 to 49·79% of strontium bromide. Strontium iodide at 25° yields a basic salt of the composition $SrI_2,2SrO,9H_2O$, which is stable in contact with solutions containing from 49·37 to 64·04% of strontium iodide.

Incidentally, the cryohydratic temperatures for strontium bromide and barium bromide were determined. The former is at $-28°$ and the eutectic solution contains 41·7% of strontium bromide. The cryohydratic temperature of the barium salt is at $-22·6°$ and the eutectic solution contains 46·6% of barium bromide.

H. M. D.

Action of Magnesium on Aqueous Solutions. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1917, **39**, 596—604. Compare this vol., ii, 90).—The action of 0·1*N*-potassium chloride has been examined on chemically pure magnesium prepared by distillation; it is shown that this solution acts just as readily on the pure magnesium as on the material previously used (*loc. cit.*), which contained 0·5% of impurity. The hydrogen-ion concentration was measured in cells of the type $Hg|Hg_2Cl_2,0·1NKCl||0·1NKCl|Pt\ H_2$, into which were placed pure magnesium and 99·5% magnesium as hydrogen generators; the hydrogen-ion concentrations were practically identical in the two cases, so that it seems safe to conclude that the impurity in the magnesium previously used did not seriously affect the results. The behaviour of magnesium (99·5%) in a series of 0·1*M*-solutions of twenty typical electrolytes was also examined in the same way as with potassium chloride, the volume of hydrogen liberated by a surface of 412 sq. cm. in twenty-four hours being measured. The general behaviour in these solutions was found to be much as in the case of potassium chloride. This is considered to be additional evidence in favour of the hypothesis already advanced that in the reaction represented by the equation $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$ the solute acts catalytically. In solutions of salts which undergo hydrolysis, the evolution of hydrogen was found to be accelerated if the base of the salt was weak and retarded if the base of the salt was strong. Non-electrolytes appear to exert no appreciable influence on the rate of reaction. This suggests that the effective catalytic agency is ionic. J. F. S.

Cerium-Iron Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1917, **99**, 25—49).—The alloys are prepared in quantities of 20 grams in special porcelain tubes, the cerium used containing 95·6% Ce, with lanthanum and traces of iron, but free from neodymium and praseodymium. Nitrogen is used to protect against oxidation. Cerium of this degree of purity freezes at 775°. The freezing-point curve falls to a eutectic point at 635° and 5% of iron. On the rising branch of the curve a compound, $CeFe_2$, separates, which is changed at 773° to the compound Ce_2Fe_5. There is a second break in the curve at 1085°, where Ce_2Fe_5 breaks up into liquid and a solid solution rich in iron. This solid solution contains up to 15% of cerium at 1085°, diminishing on cooling to about 11% at 850° and lower temperatures. It undergoes two polymorphic changes due to those of iron, at 840°, determined thermally, and again at 795°, recognised by the appearance of magnetic properties on cooling. The change in saturation of the solid solution at these points, if any, is too small to be observed. Cerium, $CeFe_2$ and Ce_2Fe_5, do not form solid solutions.

The reactions in the solid state take place slowly, and there is difficulty in obtaining equilibrium. The compound $CeFe_2$ is magnetic at the ordinary temperature, but becomes non-magnetic at 116°. It is uncertain how far the second compound is magnetic, as the alloys contain the magnetic solid solution, which becomes non-magnetic at 795°. The hardness is a maximum at 60% of cerium.

The saturated solid solution is more resistant to oxidation than pure iron. The compounds are readily oxidisable, especially $CeFe_2$. The pyrophoric properties reach a maximum at 70% of cerium, and depend on the presence of one or other of the compounds. Pyrophoric cerium alloys usually consist of a hard compound embedded in a softer, readily oxidisable ground-mass. C. H. D.

Rare Earths. EDGAR W. ENGLE and CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1917, **39**, 53—68).—A considerable quantity of a mixture of the rare earths has been fractionated first by the sodium sulphate method to remove the cerium earths from the yttrium earths and then by the bromate method to separate the yttrium earths. The bromate method is found to be efficient for concentrating erbium, yttrium, and dysprosium material. A comparative study was made of the permanganate and sulphuric acid volumetric methods for control of the fractionation. They have been found to give practically the same results in earth mixtures the bromates of which have a solubility near that of yttrium bromate. The dysprosium material obtained from the bromate fractionation was further purified by fractionation of the ethyl sulphates, and this material was very pure, and was used to determine the atomic weight of dysprosium. The method adopted consisted in the conversion of the oxide into chloride by the method used by Egan and Balke (A., 1913, ii, 508) for the atomic weight of yttrium. As a mean of six experiments, from the ratio $Dy_2O_3:2DyCl_3$ the value 164·228 was obtained for the atomic weight, which is considerably higher than the value accepted by

the international Atomic Weight Committee. Dysprosium oxide is found to have $D_{4^\circ}^{27^\circ}=7{\cdot}81$. Dysprosium chloride is described as an olive-green mass, which dissolves slowly and completely in water with development of a considerable amount of heat. The solution is almost neutral to litmus, quite neutral to methyl-orange, faintly acid to phenolphthalein and to methyl-red. J. F. S.

The Structure of Metallic Coatings Prepared by the Metallic Spraying Method. HANS ARNOLD (*Zeitsch. anorg. Chem.*, 1917, **99**, 67—72).—Coatings prepared by Schoop's method of melting the end of a rod of metal and converting the molten drops immediately into spray by the action of a blast of air have been examined microscopically. Such coatings may be obtained in an adherent form even on paper or celluloid. The molten drops are elongated during their flight through the air, so that each has a long tail. The coatings have a fine waved or laminated structure, which is characteristic, and enables them to be distinguished from coatings obtained electrolytically or by other methods. The laminæ are due to the flattening out of the drops on reaching the surface. The union of the particles is a mechanical one, the fibres being felted together, and the evidence does not point to the formation of a true weld. Thus, successive spraying with zinc and copper leaves the two metals separate, and brass is not formed. C. H. D.

Cupric Cuprous Sodium Thiosulphate Ammoniate. ALFRED BENRATH (*Zeitsch. anorg. Chem.*, 1917, **99**, 5—10).—The salt described by Bhaduri (A., 1912, i, 597) as a cuprous sodium trithionate ammoniate is deep blue, which makes it improbable that it is a cuprous salt. It is identical with a salt previously prepared by several workers from sodium thiosulphate and ammoniacal copper solutions. The cupric content of the salt is determined by making a solution out of contact with air, and comparing the colour with that of a standard cupric solution. The ratio of $Cu^{\cdot}$ to $Cu^{\cdot\cdot}$ is found to be 2 : 1. The whole of the sulphur is present in the thiosulphate complex. The number of ammonia molecules is probably five. Regarding the cupric atom as the central atom, the formula becomes:

$$\left[(Cu_2S_2O_3)Cu(NH_3)_5\right]^{S_2O_3}_{(Na_2S_2O_3)_2}.$$

It has not been found possible to prepare analogous compounds with potassium thiosulphate in place of sodium, or with ethylamine or pyridine in place of ammonia. Ethylenediamine gives a violet salt, having the composition $2CuS_2O_3,3C_2H_4(NH_2)_2,2H_2O$, in which the whole of the copper is in the cupric condition. C. H. D.

Non-aqueous Solutions. I. Reactions in *iso*Amyl Alcohol Solutions. HARRY A. CURTIS and ROBERT M. BURNS (*J. Amer. Chem. Soc.*, 1917, **39**, 33—38).—The authors have carried out a number of reactions with inorganic substances in *iso*amyl alcoholic solution. Cobalt chloride is readily soluble in *iso*amyl alcohol, forming a deep blue solution; the cobalt is only

partly precipitated by hydrogen sulphide, leaving a blue, supernatant solution. Ammonia precipitates the compound $CoCl_2,3NH_3$ as a pale rose-coloured powder. *Mercuric iodide* is only slightly soluble in cold *iso*amyl alcohol, but readily so in the hot liquid. On cooling a solution, the iodide separates in yellow crystals, which slowly pass into the red modification on keeping. Hydrogen sulphide causes the separation of an orange-red precipitate, which slowly becomes brown, and finally black if the stream of gas is continued, meanwhile, the solution takes on the odour of *iso*amyl mercaptan. If the solution is saturated with hydrogen chloride before the hydrogen sulphide is added, there is no precipitation of sulphide. *Mercuric chloride* behaves in much the same way as the iodide. *Copper chloride* forms a deep green solution, which on warming becomes brownish-green, the solution being almost opaque. Hydrogen sulphide precipitates the sulphide in a quantitative manner. Cadmium bromide added to the copper chloride turns the solution brown, owing to a double decomposition. Cadmium iodide solution precipitates cuprous iodide and liberates iodine; ammonia produces at first a green precipitate, which changes to a blue compound with more ammonia. The blue compound is unstable in the air and liberates ammonia, forming the green compound $CuCl_2,2NH_3$. Hydrogen chloride changes the colour of the solution to yellowish-brown. *Cobalt nitrate* is moderately soluble in *iso*amyl alcohol, forming a wine-red solution. The addition of hydrogen chloride changes the colour to blue; hydrogen sulphide quantitatively precipitates cobalt sulphide. Ammonia produces a dirty green precipitate. Cadmium bromide changes the colour to blue, owing to double decomposition. *Zinc chloride* is soluble in *iso*amyl alcohol to form a colourless solution. Ammonia precipitates $ZnCl_2,2NH_3$. *Cadmium iodide* solution in *iso*amyl alcohol is colourless. Hydrogen chloride liberates iodine, and ammonia precipitates $CdI_2,2NH_3$. Hydrogen sulphide precipitates a yellow compound which has the formula $CdI_2,2H_2S$. *Ferric chloride* dissolves in *iso*amyl alcohol to form an amber-coloured solution, which on keeping slowly deposits a rust-coloured precipitate. Hydrogen sulphide at first precipitates a dark brown compound, which changes to a straw-coloured compound with excess of hydrogen sulphide. *Selenium dioxide* is readily soluble in *iso*amyl alcohol, producing a solution which is acid to litmus. On keeping the solution for several days, the red modification of selenium separates out. Ammonia precipitates ammonium amyl selenite, $NH_4\cdot SeO_3\cdot C_5H_{11}$, a white compound, which on keeping in the air decomposes, red selenium separating. *Ammonium thiocyanate* is readily soluble in *iso*amyl alcohol. Hydrogen chloride precipitates ammonium chloride, and ferric chloride produces a blood-red coloration. *Methyl-orange* dissolves sparingly in *iso*amyl alcohol to form a yellow solution, which turns pink when shaken with an equal volume of $N/2$-hydrochloric acid, but when $0{\cdot}125N$-acid is used, only the aqueous layer becomes pink. The

neutral tint can be obtained in the amyl alcohol solution by using 0·2*N*-hydrochloric acid. J. F. S.

Variation in the Physical Properties of Precipitated and Colloidal Manganese Dioxide from the Point of View of Physical Chemical Equilibrium. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 25—33).—In an earlier paper (A., 1915, ii, 461) it was stated that colloidal manganese dioxide prepared from aqueous solutions of dextrose and potassium permanganate in the presence of an alkali hydroxide undergoes colloidal transformations which vary with the conditions, and seem to be dependent on equilibria of an unknown nature. It has now been shown that the amorphous colloidal manganese dioxide obtained by reducing potassium permanganate with small quantities of acetone in the presence of variable amounts of potassium hydroxide (0—155 grams per litre) undergoes changes comparable with those of the emulsoid–suspensoid type of manganese dioxide. On the basis of certain results of other workers in this field, the author has made an attempt to interpret the experimental data for both types of colloids on the basis of two types of dynamic equilibria: (1) molecular association $\rightleftarrows$ molecular dissociation, and (2) hydration $\rightleftarrows$ dehydration. The experimental observations are found to agree readily with such an interpretation.
J. F. S.

A New Method for the Passification of Iron. A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 880—884).—On the assumption that there is an internal equilibrium between ferrous and ferric ions in metallic iron, and that the passive state is to be attributed to the disturbance of this equilibrium condition in the surface layers of the metal, it was anticipated that iron would become passive in contact with a solution of a ferric salt. Since it was probable that the nitrate ion would act as a negative catalyst in regard to the internal equilibrium, experiments were made with a solution of ferric nitrate. These experiments have given a positive result—in that the iron becomes passive if the temperature does not exceed a certain value, which depends on the concentration of the ferric nitrate solution. The greater the concentration, the higher is the limiting temperature.

It is shown that the passivity cannot possibly be attributed to the free nitric acid resulting from hydrolysis of the ferric nitrate, and the observations are considered to afford further support for the authors' views on the electromotive behaviour of metals.
H. M. D.

Dialysis. II. Hot Dialysis of the Chlorides of Ferric Iron, Chromium, and Aluminium, and the Rapid Preparation of their Hydrated Oxides. MARKS NEIDLE and JACOB BARAB (*J. Amer. Chem. Soc.*, 1917, **39**, 71—81. Compare A., 1916, ii, 475, 603).—A number of experiments have been carried

out on the hot dialysis of ferric chloride and the chlorides of aluminium and chromium. The experiments were mostly carried out at 75—80° in parchment bags; two experiments were also made at the boiling point. The pure sols are obtained very rapidly. Hydrated aluminium oxide sol prepared at 75—80° is a slightly turbid and opalescent substance, from which, on keeping, a slight sediment settled. The hydrated chromic oxide sols were mobile, homogeneous, and clear green; in some cases they showed no tendency to gel after keeping for two months. The hydrated ferric oxide sols were of the yellow ochre variety; all had a tendency to settle, especially that prepared from the most concentrated ferric chloride. In very dilute solution, the whole of the ferric oxide sols were yellow, opalescent, and more stable. Pure hydrated chromic oxide sols are stable while hot, and gel slowly at the ordinary temperature. This leads to the conclusions that the higher the temperature the less electrolyte is necessary to stabilise the sol, and the attainment of adsorption equilibrium requires time at the ordinary temperature. It is also shown that the concentration of electrolyte necessary for stability at a given temperature increases with increase in the concentration of the colloid. The hydrated oxide sols have also been prepared by the addition of ammonium hydroxide to the chloride solutions and dialysing at 75—80°. The yield of colloid by this method in the case of iron is 89·9%, whilst in the case of aluminium and chromium it is only 53·3% and 41·3% respectively. This shows that in the last two cases the colloidal oxides are capable of passing through parchment paper. In the experiments conducted at the boiling point, a hydrated chromic oxide sol was obtained in ten hours which was purer than that obtained by dialysing a solution of chromic oxide in chromic chloride in the cold for seventy-three days. J. F. S.

The Hydrolysis of Cobalt and Nickel Acetate. K. A. VESTERBERG (*Zeitsch. anorg. Chem.*, 1917, **99**, 22—24).—The hydrolysis of these acetates has been determined by the extraction method (compare this vol., ii, 248). In 0·5*N*-solution at 18°, cobalt acetate is hydrolysed to the extent of 0·19% and nickel acetate to 0·43%. In 0·2*N*-solution at 18°, the hydrolysis of cobalt acetate is 0·16% and of nickel acetate 0·38%. The fact that the nickel salt appears to be more strongly hydrolysed in the 0·5*N*-solution is attributed to the salting out of acetic acid by the more concentrated solution.

Cobalt hydroxide is thus a stronger base than nickel hydroxide (compare Denham, T., 1908, **93**, 41). C. H. D.

Alkali Double Fluorides of Quadrivalent Elements. ANTON SKRABAL and JOSEF GRUBER (*Monatsh.*, 1917, **38**, 19—24). —The authors have prepared and examined a number of double fluorides of quadrivalent elements with the alkali metals. *Caesium stannifluoride*, Cs_2SnF_6, was prepared by adding a solution of

cæsium carbonate in water to a solution of a stannic acid in 40% hydrofluoric acid and allowing to crystallise. It forms hexagonal crystals, which are optically negative uniaxial and consist only of the prism [10$\bar{1}$0] and the basal plane [0001]. *Rubidium stannifluoride*, Rb_2SnF_6, was prepared similarly to the cæsium salt; it separates at first as a gelatinous mass, which becomes crystalline if kept in contact with the mother liquor for several days. It forms hexagonal tablets which are optically negative uniaxial. *Caesium plumbifluoride*, Cs_2PbF_6, was prepared by dissolving lead acetate in cold hydrofluoric acid and adding cæsium carbonate. Crystals began to separate in several days; these were rhombohedral [$a:c=1:0·7855$]. *Rubidium plumbifluoride*, Rb_2PbF_6, was prepared similarly to the corresponding cæsium compound; these crystals were also rhombohedral [$a:c=1:0·7884$). *Caesium germanofluoride*, Cs_2GeF_6, was prepared by dissolving the dioxide of germanium in hydrofluoric acid and adding a solution of cæsium fluoride. A crystalline precipitate was formed on agitating the liquid. *Rubidium germanofluoride*, Rb_2GeF_6, was formed similarly to the corresponding cæsium compound. J. F. S.

The Zirconyl Radicle (ZrO). ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 630—633).—From a study of the change in electrical conductivity of an $N/100$-solution of zirconium chloride during progressive treatment with an $N/100$-solution of sodium hydroxide, and also from measurements of the heat developed under similar conditions, the author concludes that the results obtained point to the existence of the radicle (ZrO) in zirconium compounds.
W. G.

Preparation of a Basic Bismuth Chlorate. L. VANINO and F. MUSSGNUG (*Ber.*, 1917, **50**, 323—324).—*Bismuth oxychlorate*, $BiOClO_3$, separates in long, glistening prisms on cooling a hot solution of bismuth nitrate (24·2) and sodium chlorate (96·8) in water (100). It does not react apparently when warmed with sulphur or charcoal and sulphur, but it detonates on heating with potassium cyanide. A mixture of bismuth nitrate (24) and sodium chlorate (64) gives a stable solution in 500—600 c.c. of water; such a solution is acid in reaction, but turns turmeric paper brown, this change being non-reversible, and it gives all the reactions of bismuth. Bismuth oxynitrate and chloride do not react in the same way; neither could a bromate or iodate be prepared.
J. C. W.

Preparation of Chloroplatinic Acid by Means of Hydrogen Peroxide. PAUL RUDNICK and R. D. COOKE (*J. Amer. Chem. Soc.*, 1917, **39**, 633—635).—It is shown that platinum-black dissolves entirely in a mixture of hydrochloric acid and hydrogen peroxide, forming chloroplatinic acid and thus preventing the formation of nitrosoplatinic chloride and chloroplatinous acid, two substances which very often are to be found in chloroplatinic acid prepared from aqua regia. These substances seriously affect

the accuracy of potassium estimations by means of chloroplatinic acid. The method described for the preparation of chloroplatinic acid consists in covering 10 grams of platinum-black, dried, but not ignited, with 50 c.c. of concentrated hydrochloric acid. The mixture is heated to 50—60°, and hydrogen peroxide (3—30%) slowly added at such a rate that there is moderate evolution of chlorine. J. F. S.

Mineralogical Chemistry.

The Separation and Thermal Metamorphosis of the Zechstein Salts according to the Hypothesis of Rozsa. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1917, **99**, 1—4).—The view that the potash deposits consisted primarily of kainite and bischoffite has been opposed by Rózsa (this vol., ii, 97), who maintains that kieserite and carnallite represent the primary deposit. There is no available source from which the solutions rich in magnesium chloride, required by this hypothesis, could have come. The formation of primary kainite and bischoffite is a necessary consequence of the theory of double salts, and some of the equations given by Rózsa are theoretically impossible. C. H. D.

Halloysite from Colorado. ESPER S. LARSEN and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1917, **7**, 178—180).—A white, dull, opaline clay occurs as the matrix of nodules of gearksutite in the fluor-spar mine at Wagon Wheel Gap, Colorado. It is optically isotropic with refractive index 1·47, increasing to 1·54 on exposure to air and to 1·55 after the material has been heated to 65°. Analysis agrees with the formula $Al_2O_3,2SiO_2,2H_2O,2aq$:

Al_2O_3.	CaO.	Na_2O.	SiO_2.	H_2O (below 100°).	H_2O (100—400°).	H_2O (>400°).	Total.*
35·58	0·77	0·10	40·09	8·60	2·12	12·88	100·14

* Also traces of Fe_2O_3, MgO, K_2O.

Occurring more abundantly in the same mine is another somewhat similar clay, which is also isotropic with n 1·557, but with the composition of kaolinite, $Al_2O_3,2SiO_2,2H_2O$. Halloysite is regarded as an amorphous mineral corresponding with kaolinite, but holding extra water, either by capillarity or adsorption, the formula being written as $Al_2O_3,2SiO_2,2H_2O,aq$. L. J. S.

Analytical Chemistry.

Some Main Lines of Advance in the Domain of Modern Analytical Chemistry. A. CHASTON CHAPMAN (T., 1917, **111**, 203—220).—A lecture delivered before the Chemical Society on March 15th, 1917. H. M. D.

A New Industrial Apparatus for the Estimation of Combustible Gases. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1917, **13**, 93—109).—A description of a new form of explosion pipette and absorption pipette for gas analysis. A. J. W.

Improved Nephelometer-Colorimeter. PHILIP ADOLPH KOBER (*J. Biol. Chem.*, 1917, **29**, 155—168).—The new instrument differs from the ordinary type of colorimeter, such as the Duboscq, in possessing movable cups instead of movable plungers. The heights of the cups are adjusted by means of a screw arrangement, with double milled head for rough and fine adjustment, which avoids the errors due to the lost motion inherent in racks and pinions. The plungers are made of black glass with fused-in, optically clear bottoms, and the bottoms of the cups are likewise fused in (not cemented), thus permitting the use of practically all solvents.

The author also describes a simple and convenient electric lamp with double adjustable reflectors which permit of the regulation of the amount of light reaching either side of the colorimetric field. The instrument can be furnished with an eye-support for keeping the eye steady, and also with attachable light filters for facilitating measurements with coloured fluids. Full directions for using and adjusting the instrument are appended. H. W. B.

Potassium Dichromate as a Standard. III. G. BRUHNS (*J. pr. Chem.*, 1917, [ii], **95**, 37—52. Compare A., 1916, ii, 337, 581).—Statements have been made that in the oxidation of potassium iodide solution by potassium dichromate in the presence of hydrochloric acid, the liberation of iodine sometimes occurs slowly, probably due to the intermediate formation of an iodochromate, $ICrO_3K$.

Such an observation, if real, might invalidate the use of potassium dichromate as a standard reagent, but after submitting the possibility of formation of iodochromate and of the gradual liberation of iodine to careful experimental examination, the author draws the conclusion that with dilute solutions no such danger is existent. D. F. T.

New Buffer Mixtures, Standard Tubes, and Colorimeter for Estimating the Hydrogen-Ion Concentration of Seawater. J. F. McCLENDON (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxx—xxxi; *J. Biol. Chem.*, 1917, **29**).—The two stock solutions

used are: (1) 0·3*M*-boric acid *containing* 2·25% of sodium chloride, and (2) 0·075*M*-borax solution containing 1·9% of sodium chloride. They are mixed in thirty different proportions and sealed in 'Nonsol' tubes of 24 mm. bore. Thymolsulphophthalein and *o*-cresolsulphophthalein are employed as indicators, and the comparison with sea-water, which is contained in open tubes of the same bore, is carried out with a colorimeter having the lenses of a stereoscope placed in contact so as to bring the centres of the tubes together in a sharp line when viewed from the side with one eye 6 in. from the lenses. H. W. B.

The Interference of Thiocyanates, Ferrocyanides, and Ferricyanides in the Detection of Iodides with Palladium. LOUIS J. CURTMAN and BEN R. HARRIS (*J. Amer. Chem. Soc.*, 1917, **39**, 266—270. Compare this vol., ii, 108).—Thiocyanates, ferrocyanides, and ferricyanides all interfere with the detection of iodides by means of palladium chloride. An excess of palladium favours the detection of iodides in the presence of thiocyanates. The interference due to the presence of ferrocyanides and ferricyanides can, in most cases, be overcome by boiling the reaction mixture. W. G.

Estimation of Iodine in Mineral Water and in the Thyroid Gland. D. VAN OS (*Pharm. Weekblad*, 1917, **54**, 350—353).—Chloroform employed for the extraction of iodine should be free from alcohol. The difficulty is avoided by employing carbon disulphide or tetrachloride. A. J. W.

Iodometric Estimation of Sulphur Dioxide and the Sulphites. JOHN B. FERGUSON (*J. Amer. Chem. Soc.*, 1917, **39**, 364—373).—The author has made a critical experimental examination of the methods in general use for the estimation of sulphur dioxide in gas mixtures. For the very exact estimation of large or small amounts of sulphur dioxide, the excess iodine method is recommended. For small amounts only, either the excess iodine method or the Selby Smelter Commission method should be used, depending on which is the more convenient under the given working conditions. The Reich method may be used for either small or large amounts, but will yield accurate analyses only when sufficiently large samples are taken to render the uncertain end-point a negligible source of error. When carbon dioxide and sulphur dioxide are to be estimated in the same sample, the sulphite method can be used to advantage. With mixtures not above 3 or 4%, a suitable correction factor will render the results fairly accurate, but with higher concentrations the uncertainty increases. The author emphasises the following points to be observed in gas volumetric analysis: (1) The gas must nowhere come in contact with moisture prior to its reaching the absorbent. (2) The apparatus must be free from all rubber connexions when exact analysis of mixtures containing more than 10% of sulphur

dioxide are to be made. For very accurate work, it is better to dispense with rubber entirely, although this source of error for mixtures containing less than 3% of sulphur dioxide may be neglected. (3) Mixtures of sulphur dioxide and air when dry do not interact appreciably, but when moist slow oxidation takes place. For this reason it is impossible to recover from a moist gas holder, even by pumping, the initial amount of sulphur dioxide if the gas has been kept for any great length of time. The author recommends the following procedure for the analysis of such soluble sulphites as sodium sulphite. The solid salt is dissolved directly in an excess of an iodine solution containing sufficient hydrochloric acid, and the excess iodine is estimated with thiosulphate. This eliminates several sources of error due to oxidation of the salt by agents other than the iodine solution. J. F. S.

Detection and Estimation of Small Quantities of Free Sulphuric Acid in the Presence of Sulphates. E. VULQUIN and M. ENTAT (*Ann. Chim. anal.*, 1917, **22**, 61—66).—Measurements are made of the conductivity of the solution while it is titrated with barium hydroxide solution; the burette readings are plotted against the conductivity figures, and the curve exhibits an inflexion at the point where the free sulphuric acid has been neutralised. The differences in potential are measured between a rotating polarised platinum electrode and a normal calomel electrode, both placed in the solution (compare Dutoit and von Weisse, A., 1911, ii, 1129). The method is suitable for estimating quantities of 0·005 gram of sulphuric acid in the presence of sulphates, organic acids, and mineral and organic salts. W. P. S.

New Reagent for the Separation of Ammonia. I. Colorimetric Estimation of Ammonia in Urine. OTTO FOLIN and RICHARD D. BELL (*J. Biol. Chem.*, 1917, **29**, 329—335. Compare Folin and Denis, A., 1916, ii, 574).—The authors recommend "permutit" as a substitute for Merck's purified blood charcoal in the method for the estimation of ammonia previously published. Permutit absorbs the ammonia from neutral or slightly acid solutions, and the permutit–ammonia compound is decomposed on Nesslerisation with the production of the normal colour. The permutit may be collected, washed, and used again repeatedly.
H. W. B.

Micro-titration of Ammonia. GEORGE D. BARNETT (*J. Biol. Chem.*, 1917, **29**, 459—462).—See this vol., i, 359.

"Nitron" as a Gravimetric Reagent for the Analysis of Substances used in Explosives. W. C. COPE and J. BARAB (*J. Amer. Chem. Soc.*, 1917, **39**, 504—514).—For the most part a summary of previous work on the use of "nitron" as a precipitant in the estimation of nitric acid, perchloric acid, picric acid, and their salts, a full bibliography being given. The use of "nitron" has been extended to the estimation of trinitrocresol and its salts

under conditions similar to those for picric acid (compare Busch and Blume, A., 1908, ii, 328). In the presence of sulphuric acid, dinitrophenol does not give a precipitate with "nitron," this forming the basis for a simple method for the estimation of mixtures of di- and tri-nitrophenols. Busch's method for estimating "nitrocellulose" (compare A., 1906, ii, 708) can be used for "nitromannitol" and "nitrostarch," but for "nitroglycerin" it is necessary to use 30% hydrogen peroxide. W. G.

The Volumetric or Pemberton Method for Estimating Phosphoric Acid, with some Experiments showing the Influence of Temperature and the Sulphuric Acid Radicle on the Results. PHILIP McG. SHUEY (*J. Ind. Eng. Chem.*, 1917, **9**, 367—370).—Very varying results are obtained, according as the precipitation is carried out at various temperatures over the range 5—65°. The most satisfactory conditions are to precipitate at 30°, the molybdic acid solution added being also at that temperature. It is advisable when precipitating from a sulphuric acid solution to add at least 5 grams of ammonium nitrate. Old molybdate solutions from which molybdic acid tends to separate should not be used, as they seriously affect the results. W. G.

Detection of Carbon in Inorganic and Organic Substances. ERNST MÜLLER (*J. pr. Chem.*, 1917, [ii], **95**, 53—54).—A mixture of approximately 0·02 gram of the substance under investigation with roughly twenty times its weight of potassium azide is cautiously heated, at first gently and then, finally, for two minutes at a red heat. Potassium cyanide is formed, and may be recognised in the usual way by conversion into Prussian blue.

The test, which may be rendered still more delicate by the additional presence of a little metallic potassium in the reaction mixture, can not only be applied to organic compounds, but also to steel and carborundum. D. F. T.

The Penfield Test for Carbon. W. G. MIXTER and F. L. HAIGH (*J. Amer. Chem. Soc.*, 1917, **39**, 374—375).—The authors describe a test, due to S. L. Penfield, for the detection of carbon in minerals and metals. The method consists in heating an intimate mixture of lead chromate and the substance in a narrow, horizontal, hard glass tube which has a small bulb blown in the underside of it near the open end. In the experiment, this bulb contains a drop of a saturated solution of barium hydroxide. The formation of a white film of barium carbonate on the liquid indicates the presence of carbon in the substance. The lead chromate is prepared by precipitation, and any accidental admixture of carbon from dust is removed by heating it in oxygen in the tube before the experiment. A series of experiments is described. A mixture of 9·990 grams of alumina and 0·010 gram of silicon carbide was made, and various quantities of this were mixed with the lead chromate and the test carried out. It is shown that 10 mg.

of the mixture, corresponding with 0·003 mg. of carbon, gave a definite reaction. J. F. S.

A Colorimetric Method for the Estimation of the Percentage of Carbon Dioxide in the Air. H. L. HIGGINS and W. MCKIM MARRIOTT (*J. Amer. Chem. Soc.*, 1917, **39**, 68—71). —A rapid method of estimating the amount of carbon dioxide in the air is described. The method consists in blowing the air through 2—3 c.c. of 0·001*N*-sodium hydrogen carbonate solution containing 0·01% of phenolsulphonephthalein until the colour has reached a constant tint. This tint is then compared with a series of comparison tints made by mixing suitable quantities of potassium dihydrogen phosphate and disodium hydrogen phosphate in test-tubes, adding 0·01% solution of phenolsulphonephthalein, and sealing. The method gives an accuracy of 5%. For air containing larger amounts of carbon dioxide than ordinary air, a solution of 0·0085*N*-sodium hydrogen carbonate is used. The results are deduced directly in parts per 10,000 from figures placed on the standards. The method is inapplicable in air containing ammonia or acid fumes. J. F. S.

Estimation of Carbon Dioxide in Carbonates by Diminished Pressure. JOHN B. ZINN (*J. Amer. Chem. Soc.*, 1917, **39**, 270).—The usual apparatus is connected in series with an 8-litre aspirating bottle provided with a stopcock, which is opened before adding the acid to the reaction flask, thereby causing a slight fall in the pressure. The flow of gas is regulated by means of a stopcock in the dropping funnel, and ceases automatically when the aspirator is empty of water. H. M. D.

[Titration of] Alkalis and Ammonia by Oxalic Acid and Methyl-orange. G. BRUHNS (*Chem. Zeit.*, 1917, **41**, 189).—The author, after a general discussion of the utility and trustworthiness of oxalic acid as a starting material in volumetric analysis, describes methods by which alkali hydroxides, ammonia, and borax can be estimated by means of oxalic acid and methyl-orange. In the case of alkalis, the oxalic acid is titrated with the alkali until the end-point is almost reached, then calcium chloride sufficient to precipitate the whole of the oxalic acid is added. Methyl-orange is then added, and the titration completed. The calcium chloride may be replaced by zinc sulphate, lead nitrate, silver nitrate, and other salts which are neutral to methyl-orange. The same process may be applied to the estimation of borax with equally good results. In the case of ammonia, it is advisable to add 30—40 grams of boric acid to each litre of *N*/10-ammonia to prevent the loss of ammonia by evaporation; otherwise, the process is as described above. J. F. S.

The Estimation of Potassium as Perchlorate. GREGORY P. BAXTER and MATSUSUKE KOBAYASHI (*J. Amer. Chem. Soc.*, 1917, **39**, 249—253).—The use of alcohol saturated with potassium

perchlorate for washing the precipitated salt, as recommended by Davis (compare T., 1915, **107**, 1678), has been found to give greatly increased accuracy in this method of estimation. In presence of sodium, the precipitate tends to retain sodium perchlorate, but this source of error may be avoided by adopting Caspari's suggestion (A., 1893, ii, 390), that the precipitate should be redissolved after a preliminary washing and the potassium perchlorate reprecipitated. The authors' experience also suggests the use of absolute alcohol at a low temperature (0°) in the washing operations, and also the use of a platinum-sponge crucible.

H. M. D.

Rapid Method for Estimating Calcium in Blood and Milk. HENRY LYMAN (*J. Biol. Chem.*, 1917, **29**, 169—178).—The method previously described (A., 1915, ii, 700) for estimating calcium in urine and fæces has been modified so as to permit of its estimation in blood and milk. Only 5 c.c. of blood or milk are required for an estimation which takes about two hours to complete. The proteins are removed by precipitation with trichloroacetic acid, and the calcium then precipitated by ammonium stearate as a fine cloud, which is compared with the turbidity of a standard solution in a nephelometer. The results are stated to be accurate to within less than 1%. H. W. B.

Titration of Magnesium. F. W. BRUCKMILLER (*J. Amer. Chem. Soc.*, 1917, **39**, 610—615).—The author has examined two methods of volumetric estimation of magnesium in water, and gives details of the more favourable method of procedure. (1) After calcium has been removed, the solution containing magnesium is evaporated to dryness and the ammonium salts are expelled by ignition. The residue is taken up with water, acidified with hydrochloric acid, and, after filtering, made slightly alkaline with ammonium hydroxide. Microcosmic salt solution is slowly added to the cold solution with stirring, and, after the precipitate has formed, a volume of ammonia, equal to one-third of the total volume, is added and the solution kept for eighteen hours. The precipitate is filtered with suction and washed with 25 c.c. of alcohol. The precipitate is then washed into a beaker, a known excess of $0{\cdot}1N$-hydrochloric acid is added, and the excess of acid titrated with $0{\cdot}1N$-sodium hydroxide, using methyl-orange as indicator. (2) The solution from the calcium precipitate is evaporated to dryness and ignited. The residue is taken up in acidified (HCl) water, heated, and filtered. The filtrate is treated with an excess of 10 c.c. of aqueous ammonia and an excess of 10—20% of sodium arsenate. The solution is cooled and stirred for ten minutes. The precipitate is collected and washed with 3% ammonia water. It is then placed in an Erlenmeyer flask fitted with a trap, and boiled with 10 c.c. of 1 : 1-sulphuric acid and an excess of potassium iodide until iodine vapours are no longer visible. While still hot, the remaining traces of iodine are destroyed by sulphurous acid and the whole

cooled quickly. The acid solution is neutralised with $0{\cdot}1N$-sodium hydroxide, using phenolphthalein as indicator, and adding from time to time sodium phosphate solution. When titration is complete, the volume of phosphate solution added should be one-half the volume of the iodine solution. The arsenious oxide solution is then titrated with $0{\cdot}1N$-iodine solution. J. F. S.

Titration of some Bivalent Metal Sulphates by the Conductance Method. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1917, **39**, 252—266).—It is shown that the change in the electrical conductivity of solutions containing sulphates of certain metals, on the addition of a solution of barium hydroxide, affords a method for the estimation of the metals in question. The apparatus employed permits of the measurements being carried out in an atmosphere containing carbon dioxide.

The method is applicable to the estimation of magnesium, copper, nickel, and cobalt in solutions containing the respective sulphates. It may also be used in the estimation of magnesium in a solution containing magnesium sulphate, calcium sulphate, and sulphuric acid, and hence is suitable for the estimation of magnesium in a dolomite. Results obtained with cadmium sulphate indicate the formation of a basic sulphate of the composition $CdSO_4,3Cd(OH)_2$. H. M. D.

Method for the Separation of Lead and Iron. J. F. SACHER (*Chem. Zeit.*, 1917, **41**, 245).—The process depends on the insolubility of basic ferric nitrate; it is useful for the separation of very small amounts of iron from lead salts. Two grams of the lead salt containing iron are heated on a water-bath with an excess of nitric acid (D 1·15), the mixture is then evaporated, and the residue heated at 100° for about fifteen minutes. The residue is now treated with hot water, the insoluble portion collected on a filter, washed, then dissolved in hot dilute hydrochloric acid; the iron is precipitated from this solution as hydroxide by the addition of ammonia, and the precipitate is collected, washed, ignited, and weighed. If the substance under examination contains silicates which are decomposed by nitric acid, the residue obtained after the evaporation of the nitric acid must be heated at 125°; lead nitrate does not undergo the slightest decomposition at this temperature. Should lead sulphate be present, the residue is extracted with ammonium acetate solution before the basic iron salt is dissolved in hydrochloric acid. W. P. S.

Detection of Traces of Mercury Salts for Toxicological Purposes. KENDALL COLIN BROWNING (T., 1917, **111**, 236—240). —The method described, a development of the Dupré method of detecting mercury in explosives, involves the electrolytic deposition of the mercury on a gold cathode, which is then washed with water and introduced into a Dupré tube heated at 200—250°, the mercury being detected by its spectrum. The best conditions for

electrolysing the mercury solution and for making the spectroscopic observations have been determined as the result of systematic tests.

It was found that the mercury spectrum is shown when 200 c.c. of a solution containing one part of mercuric chloride in a thousand million is electrolysed for ten minutes, using a current of two amperes.

Very dilute solutions of mercuric salts show a loss of mercury when kept in soft glass or even in ignited quartz glass bottles. If such solutions are evaporated with the object of concentrating the mercury salts, there is also a very appreciable loss.

H. M. D.

Estimation of Mercury in Basic Mercuric Salicylate and its Isomerides. H. Lajoux (*J. Pharm. Chim.*, 1917, [vii], **15**, 241—246).—Rupp has shown (A., 1901, ii, 348) that the mercury in mercury salicylate in hydrochloric acid solution is not converted into mercury sulphide by treatment with hydrogen sulphide, and that only when the mixture is heated at 100° does the formation of sulphide take place; even then the action is very slow and attended with risk of incomplete decomposition of the intermediate compound which is first formed. The following method, in which the salicylate is decomposed with potassium cyanide, is therefore recommended. A weighed quantity of 0·25 gram of the mercury salicylate or of its isomerides is mixed with 1·25 grams of potassium cyanide and 25 c.c. of water, the solution is heated, and saturated with hydrogen chloride, care being taken not to inhale the vapours given off at this stage of the process. The solution is now diluted with boiling water to about 150 c.c., and, while hot, treated with a current of hydrogen sulphide. The mercury is precipitated completely as sulphide within a few minutes, and the precipitate is collected, washed, and weighed. The mercury may also be estimated volumetrically after the salicylate has been decomposed by sulphuric acid or aqua regia. One gram of the substance is heated on a water-bath for a few minutes with 10 c.c. of concentrated sulphuric acid, and the violet solution is diluted to 100 c.c.; or the same quantity of the substance is boiled with 4 c.c. of hydrochloric acid and 2 c.c. of nitric acid, potassium chlorate is added, and the colourless mixture then diluted to 100 c.c. Twenty c.c. of the solution (obtained by either of these treatments) are then added to a flask containing 10 c.c. of ammonia, 10 c.c. of $N/10$-potassium cyanide solution, 1 c.c. of 10% potassium iodide solution, and 60 c.c. of water, and the mixture is titrated with $N/10$-silver nitrate solution until a persistent opalescence is obtained. The quantity of mercury present is calculated from the volume of silver nitrate solution used. Approximately one-half of the quantity of mercury is found if the salicylate is dissolved directly in potassium cyanide solution, then treated with ammonia, potassium iodide, and water, and the solution titrated with silver nitrate solution. Basic

mercuric salicylate should contain 59·52% of mercury, but commercial samples rarely contain more than 57%. W. P. S.

Differential Iodometry. III. Estimation of the available Oxygen in Soluble and Precipitated Oxidised Forms of Manganese. O. L. BARNEBEY and W. C. HAWES (*J. Amer. Chem. Soc.*, 1917, **39**, 607—610. Compare following abstract).—Methods are described for the estimation of the available oxygen in commercial permanganates, precipitated highly oxidised manganese oxides, and some forms of pyrolusite, all of which contain some iron. In the case of potassium permanganate containing ferric sulphate, 10 c.c. of *N*-potassium iodide and 10 c.c. of 2*N*-phosphoric acid are added, the mixture is allowed to react for three minutes, and the iodine titrated with thiosulphate. The results are extremely good. With precipitated oxides of manganese, and such samples of natural pyrolusite as do not contain much iron, the weighed sample is treated with 10 c.c. of *N*-potassium iodide and 10 c.c. of 2*N*-phosphoric acid, and kept at the ordinary temperature for fifteen minutes. Then the liberated iodine is titrated with sodium thiosulphate. The estimations were controlled by the Bunsen distillation method, and an extremely good agreement between the two values obtained. In cases of pyrolusite which contains much iron, the reaction takes place very slowly and does not easily go to completion, hence the method is not to be recommended in such cases. J. F. S.

Differential Iodometry. II. The Titration of Chromic Acid in the Presence of Ferric Iron and the Analysis of Chromite for its Chromium Content. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1917, **39**, 604—606. Compare A., 1915, ii, 574; 1916, ii, 261).—A method has been worked out for the iodometric estimation of chromic acid in the presence of ferric iron. An aqueous solution of the sample is made just alkaline with sodium hydroxide, then solid sodium peroxide is added in slight excess. The solution is boiled for a few minutes to decompose the excess of peroxide, and it is then made acid with phosphoric acid, a sufficient excess of which is added to dissolve completely the ferric phosphate and make the solution about 3*N*-phosphoric acid. Ten c.c. of *N*-potassium iodide are added for every 100 c.c. of solution, and the liberated iodine is titrated with sodium thiosulphate. In this reaction the whole of the liberated iodine is due to the chromic acid, since the ferric phosphate is only slightly ionised and its velocity of reaction with potassium iodide is very small. The analysis of chromite is conducted as follows. A sodium peroxide fusion is made; this is extracted with water and the solution boiled. The solution is acidified with sufficient excess of phosphoric acid to make a 3*N*-solution, potassium iodide is added, and the liberated iodine titrated with thiosulphate. The results of several analyses are given, in which the chromium has been estimated both gravimetrically and volumetrically; the agreement between the two estimations is extremely good. J. F. S.

The Estimation of Molybdenum by Potassium Iodate. GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1917, **39**, 246—249).—It is shown that molybdenum in the form of molybdate may be accurately estimated by the use of iodic acid. The molybdate solution, acidified with hydrochloric acid, is heated to 50° and allowed to pass slowly through a column of amalgamated zinc into a 500 c.c. flask containing 5 c.c. of iodine monochloride solution, 25 c.c. of concentrated hydrochloric acid, 5 c.c. of water, and 7 c.c. of chloroform, the flask being cooled by immersion in a bath of cold water. The liquid is then titrated with potassium iodate, the reaction taking place corresponding with the equation $KIO_3 + Mo_2O_3 + 2HCl = KCl + Mo_2O_5 + ICl + H_2O$. The end-point is quite sharp, although the rapid reaction in question is followed by a relatively slow reaction, in which the molybdenum is oxidised to MoO_3. To prevent hydrolysis of the iodine monochloride it is important that the solution in the flask should contain not less than 10% of hydrochloric acid. H. M. D.

Alleged Ninhydrin Reaction with Glycerol, etc. VICTOR JOHN HARDING (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiv; *J. Biol. Chem.*, 1917, **29**).—The author finds that specimens of glycerol of different origin behave differently towards ninhydrin, and concludes that a positive ninhydrin reaction with glycerol is really due to the presence of nitrogenous impurities. H. W. B.

Estimation of Cholesterol in Blood. W. R. BLOOR (*J. Biol. Chem.*, 1917, **29**, 437—445. Compare Weston, this vol., ii, 156).—The author discusses possible reasons for the inconsistency of the results obtained by Weston for the cholesterol in blood estimated by Bloor's method. H. W. B.

Cholesterol. III. Influence of Bile Derivatives in Bloor's Method of Estimation of Cholesterol. GEORGINE LUDEN (*J. Biol. Chem.*, 1917, **29**, 463—476).—A modified Liebermann reaction for cholesterol is given by cholesterol-free gall-stones. The difference in the results afforded by Bloor's original and his modified methods for the estimation of cholesterol (A., 1916, i, 176; ii, 275) is probably due to the participation in the latter method of biliary pigments and acids in the reaction. The figures given by the modified method are always higher, and the difference between the results obtained by the two methods may possibly furnish useful information in cases of biliary disturbance with or without jaundice. H. W. B.

Separation of Cholesterol and Phytosterol from Fats and Oils by means of Digitonin. J. PRESCHER (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 77—80. Compare A., 1916, ii, 499).—The digitonin reagent used should contain 1% of the substance in 96% (by vol.) of alcohol; two kinds of digitonin are sold, one being a crystalline substance which is insoluble in water, whilst the other is amorphous and soluble in water. The former is the better precipitant for cholesterol and phytosterol. In place of chloroform, ether, etc., other solvents, such as dichloroethylene, perchloro-

ethylene, or pentachloroethane, might be employed to remove the fat from the digitonin precipitate, but their suitability for the purpose requires proof. W. P. S.

A New Reaction Distinguishing the Sugars. LUIS GUGLIALMELI (*Ann. Soc. Quim. Argentina*, 1916, **4**, 277—282).—An application of Sánchez's fluorescent reaction to distinguish sugars (*ibid.*, 1915, **3**, 305). A. J. W.

Improved Method of Estimating Sugar in the Urine and Blood. P. J. CAMMIDGE (*Lancet*, 1917, i, 613—614).—The author finds the iodometric estimation of sugar by Scales's method (A., 1916, ii, 117) to be both accurate and rapid, and applies it to a modified Benedict solution, which is ten times as sensitive to reducing sugars as Fehling's solution, and keeps indefinitely. Details for the estimation of sugar in urine and blood are given; of the latter, 0·1—0·2 c.c. suffices. G. B.

Thiobarbituric Acid as a Qualitative Reagent for Ketohexose. G. P. PLAISANCE (*J. Biol. Chem.*, 1917, **29**, 207—208).—The substance to be tested is placed in a test-tube and sufficient hydrochloric acid and water are added to bring the acid concentration to 12%. The tube is heated over a free flame until boiling begins. It is then cooled and a few drops of a thiobarbituric acid solution in 12% hydrochloric acid are added. If a ketohexose was originally present, an orange-coloured precipitate forms on keeping. If only aldoses are present, the solution may become yellow, but a precipitate is not formed. Barbituric acid cannot be used instead of thiobarbituric acid, because the condensation product is much more soluble. When larger concentrations of hydrochloric acid are employed, slight precipitates may also be obtained from aldoses. H. W. B.

The Determination of the Gelatinisation Temperatures of Starches by means of an Electrically Heated Chamber on the Microscope Stage. ARTHUR W. DOX and G. W. ROARK, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 742—745).—A slight modification of the method of Francis and Smith (compare *J. Ind. Eng. Chem.*, 1916, **8**, 509), the hot water circulating device being replaced by an electric incubator for the microscope stage. The necessary temperature correction was ascertained by determining in the apparatus the melting points of three organic substances, the melting points of which cover the range of gelatinisation temperatures. The gelatinisation temperatures of the starches from a large number of different varieties of maize were determined, and, whilst no difficulty was found in getting concordant results for a given variety, the results varied between 64·1° and 71·1° for the different sorts. W. G.

Nitrogen in Amino-form as Estimated by Formaldehyde-titration, in Relation to some other Factors Measuring Quality in Wheat Flour. C. O. SWANSON and E. L. TAGUE (*J. Amer. Chem. Soc.*, 1917, **39**, 482—491).—Estimations of ash, acidity, total nitrogen, and nitrogen in amino-form

as given by the formaldehyde titration (compare Sorensen, *J. Amer. Chem. Soc.*, 1916, **38**, 1098) have been made on a number of samples of flour collected from different mills and also on one set of mill-stream flours from a medium-sized mill. The results show that nitrogen in amino-form, as measured by the formaldehyde-titration, is valuable, together with the ash and acidity, in measuring quality in flour. It should be noted, however, that titratable nitrogen is more uniformly distributed in the wheat kernel than are the materials which determine the amount of ash and acidity. The increase in titratable nitrogen is, therefore, not proportionate to the increase in ash or acidity in clear and low-grade flours, as compared wth patent and straight flours made from the same sound wheat. W. G.

The Duclaux Method for the Estimation of the Volatile Fatty Acids. FRED. W. UPSON, H. M. PLUM, and J. E. SCHOTT (*J. Amer. Chem. Soc.*, 1917, **39**, 731—742).—The authors have redetermined the Duclaux constants (compare A., 1896, ii, 504) for formic, acetic, and propionic acids and do not find close agreement. Working with mixtures of these acids, it is found that small, unavoidable experimental errors may vitiate the results, that when more than two acids are present in a mixture almost identical series of results may be calculated from mixtures of the acids in quite different proportions, and further, that results which, from the constants, indicate the presence of only one acid, may just as well be calculated in terms of three or more acids. Small amounts of acids in a mixture may just as well be distributed between the acids next higher and lower in the series. W. G.

The Duclaux Method for Volatile Fatty Acids. A. R. LAMB (*J. Amer. Chem. Soc.*, 1917, **39**, 746—747).—Contrary to the conclusions of Upson, Plum, and Schott (preceding abstract), the author considers that accurate results can be obtained with Duclaux's method, working under carefully defined conditions and using electrical heating for the distillation, provided that no attempt is made to determine more than two or three acids in the same fraction. The main essential is to use highly purified acids for the preliminary determination of the constants.

W. G.

Studies in Steam Distillation. Some Applications of Duclaux's Method. H. DROOP RICHMOND (*Analyst*, 1917, **42**, 133—138).—Duclaux's method is trustworthy for the estimation of butyric acid in acetic anhydride, and it is shown that a combination of the usual titration methods and the Duclaux method will give the quantities of acetic anhydride, acetic acid, and butyric acid present in a sample. An examination of the acid obtained by hydrolysis of the acetanilide formed would indicate what proportion of the butyric acid was present as anhydride. Acetyl chloride may be examined in the same way; samples of this substance examined by the author did not contain butyric acid. Duclaux's method is also suitable for testing the purity of substituted malonic acids. W. P. S.

Separation and Estimation of Butyric Acid in Biological Products. I. I. K. Phelps and H. E. Palmer (*J. Biol. Chem.*, 1917, **29**, 199—205).—The authors find that butyric acid can be separated from mixtures containing formic, acetic, and butyric acids by means of the solubility of quinine butyrate and the insolubility of quinine acetate and quinine formate in carbon tetrachloride. The actual amount of butyric acid may be estimated by weighing the quinine butyrate, which may be crystallised and identified by its melting point (77·5°). The solubilities of the quinine salts of propionic and butyric acids in carbon tetrachloride are too similar to allow of a separation being effected by fractional crystallisation. H. W. B.

The Identification and Estimation of Lactic Acid in Biological Products. I. K. Phelps and H. E. Palmer (*J. Amer. Chem. Soc.*, 1917, **39**, 136—149).—The lactic acid is esterified by means of alcohol vapour containing dry hydrogen chloride passed through the mixture containing the lactic acid, suspended in vaselin at 100—110°, using zinc chloride as a second catalyst. The ethyl lactate passes over along with any other esters of low boiling point, whilst esters such as the citrate and tartrate remain in the flask. The distillate is fractionally distilled through a Hempel column, any ethyl formate and acetate, together with a large proportion of the propionate and butyrate present, being thus removed. The residue in the flask which contains the ethyl lactate is hydrolysed with barium hydroxide, and the acids converted into their quinine salts. Quinine lactate is separated from the butyrate and propionate by reason of the much greater solubility of the latter salts in carbon tetrachloride. The quinine lactate is weighed and identified by its melting point. It is essential, in this estimation, that the aqueous solutions of quinine lactate should not be allowed to remain, and especially that they should not be heated, but should be evaporated by distillation under diminished pressure. If this precaution is not observed, quinotoxine lactate may be formed, and this is much more soluble in carbon tetrachloride than quinine lactate.

In the absence of propionic and butyric acids, lactic acid may also be estimated as guanidine lactate. W. G.

Influence of Calcium Tartrate on the Estimation of Total Tartaric Acid (in Crude Tartars). P. Carles (*Ann. Chim. anal.*, 1917, **22**, 71—72).—The Goldenberg method sometimes gives low results when applied to crude tartars containing a large proportion of calcium tartrate; this is probably due to incomplete decomposition of the calcium tartrate during the treatment with potassium carbonate. It is recommended that the hydrochloric acid solution of the sample should be added gradually, with constant stirring, to the potassium carbonate solution, and the mixture then boiled until all hydrogen carbonates have been decomposed; the mixture should now be alkaline to phenolphthalein. The presence of undecomposed calcium tartrate is

indicated if the separated and washed calcium carbonate is not completely soluble in acetic acid. W. P. S.

A Method for the Examination of Methyl Salicylate. ALAN R. ALBRIGHT (*J. Amer. Chem. Soc.*, 1917, **39**, 820—825).—In examining a sample of methyl salicylate, it is first benzoylated, thus converting the true methyl salicylate and any other phenolic substances present into crystalline benzoates. The crystalline product is mounted on an object slide, using a liquid equal in refractive index to the mean index of methyl *o*-benzoyloxybenzoate. Then, when examined with a petrographic microscope, the salicylate derivative becomes invisible, leaving other compounds in clear view, thus facilitating their identification by means of their optical properties. Using this method, phenol has been found both in synthetic and pure, natural methyl salicylate. In some synthetic methyl salicylates, the methyl ester of *p*-hydroxytoluic acid has been detected in very small amount, but not in the natural oil. A substance closely resembling methyl *p*-hydroxybenzoate also occurs in the synthetic ester, but not in genuine oils of wintergreen or birch. W. G.

Quick Titration Method for Estimating Small Amounts of Uric Acid. J. LUCIEN MORRIS (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiii; *J. Biol. Chem.*, 1917, **29**).—The uric acid is separated from the urine, blood, or other fluid by precipitation as zinc urate, and is then titrated in acetic acid solution with $N/200$-potassium permanganate solution. H. W. B.

Value of the Determination of the Freezing-point in the Examination of Milk. J. J. POLAK (*Chem. Weekblad*, 1917, **14**, 323—324).—The author considers that the freezing-point method affords the most trustworthy test for the presence of water in milk. A. J. W.

Titration Method for Estimating Minute Quantities of Acetone. ROGER S. HUBBARD (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiv; *J. Biol. Chem.*, 1917, **29**).—The modification of the Messinger method described by the author consists chiefly in the employment of standard solutions of iodine and thiosulphate of $N/100$- or $N/500$-strengths. H. W. B.

[Estimation of Creatinine and Total Creatinine (Creatinine and Creatine) in Whole Blood]. D. WRIGHT WILSON and E. D. PLASS (*J. Biol. Chem.*, 1917, **29**, 413—423).—See this vol., i, 360.

The Qualitative Identification of the Drugs containing Emodin. GEORGE D. BEAL and RUTH OKEY (*J. Amer. Chem. Soc*, 1917, **39**, 716—725).—The authors have devised a tentative scheme for the identification of the drugs cascara, rumex, rhubarb, frangula, senna, and aloes.

A small amount of a dilute alcoholic solution of the drug preparation is shaken with four times its volume of benzene. A small portion of the benzene extract is shaken with 30% aqueous sodium hydroxide, when a permanent coloration varying from light red to deep violet is obtained if one of the drugs is present. If the test is positive, another portion of the benzene extract is evaporated to dryness, moistened with concentrated nitric acid, and evaporated again. The residue will be red or orange-red, and when moistened with a solution of potassium cyanide in potassium hydroxide will become red or purplish-red if one of the drugs is present.

For the identification of the individual drug, one portion of the alcoholic solution is shaken with four volumes of benzene, the benzene extract drawn off, and the extraction repeated with amyl alcohol. Another portion of the dilute alcoholic solution is extracted with ethyl ether. A portion of the benzene extract is shaken with concentrated aqueous ammonia, a deep reddish-violet colour and precipitate indicating the presence of rhubarb, which may be confirmed by shaking another portion of the benzene extract with lead subacetate, a yellowish-orange precipitate turning red with alkali confirming the presence of rhubarb.

A portion of the amyl alcohol extract is shaken with strong aqueous ammonia. A deep red colour with a dark green fluorescence indicates aloes or a freshly prepared extract of cascara. If the test is positive, another portion is shaken with mercurous nitrate; a red colour in the aqueous layer indicates aloes, which may be confirmed by the cupraloin test (compare Klunge, *Chem. Zeit.*, 1880, **4**, 1085), the hydrogen peroxide test (compare Hirschsohn, *Pharm. Zentr.*, 1901, **42**, 63), or the fluorescence test with borax. The presence or absence of cascara may be proved by evaporating a portion of the benzene or amyl alcohol extract, nitrating, and treating with stannous chloride. Cascara will give a deep red colour, aloes a yellowish-brown.

A portion of the ether extract is shaken with an equal volume of saturated nickel acetate solution, when a red, aqueous layer indicates senna. If the solution retains its green colour and gives a green precipitate with potassium hydroxide, rumex is present. If on shaking this mixture with potassium hydroxide a violet precipitate is formed, senna is indicated, whilst with rhubarb or frangula it will be reddish-violet, and with cascara dark orange-red.

If the above tests are not conclusive, a portion of the ether extract is evaporated, nitrated, and reduced with stannous chloride at 100°. Senna gives a green residue, aloes a brown one, cascara red, rumex, rhubarb, and frangula violet-red, frangula being the deepest. The residues are washed with water to remove the stannous chloride, and a drop of sodium hypochlorite solution added. Senna alone develops a distinct red colour, the others turning yellow before decolorisation. W. G.

General and Physical Chemistry.

Absolute System of Colours. II. WILHELM OSTWALD (*Zeitsch. physikal. Chem.*, 1917, **92**, 222—226. Compare A., 1916, ii, 205).—The general equation expressing colour in the author's system involves three terms connected by the relation $r+w+s=1$, where r refers to a pure colour, w represents white, and s black. The determination of the pure colour factor r in terms of the frequency of light in the visible spectrum is discussed, and a table is given showing the relation between the frequency and the classification of the various colours according to the author's system.

H. M. D.

Determination of the Spectrum of a Univalent Polyatomic Ion, and in Particular of the $H^{\cdot}_2$ Ion. J. STARK (*Ann. Physik*, 1917, [iv], **52**, 221—254).—In a further attempt to differentiate the carriers which are responsible for the spectra which are emitted under different conditions, it has been found that the many-lined spectrum of hydrogen is to be attributed to diatomic hydrogen ions carrying a single positive charge. The spectrum in question is excited in greater intensity by low-speed cathode rays (20—50 volts), whereas the canal rays give rise to a very feeble emission of the many-lined spectrum. It is not yet known whether the visible spectrum attributable to the $H_2^{\cdot}$ ions is accompanied by a characteristic emission in the ultra-red or in the ultra-violet.

The above-mentioned spectrum of the univalent diatomic hydrogen ion is discussed in reference to the spectra emitted by the univalent, monatomic hydrogen ion, the hydrogen atom, and the hydrogen molecule.

H. M. D.

The Emission of a Continuous Spectrum in the Combination of an Electron with a Positive Ion. J. STARK (*Ann. Physik*, 1917, [iv], **52**, 255—275).—The fact that hydrogen gives rise to a continuous spectral emission in the near ultra-violet has been noted by several observers, but the conditions under which this is obtained have not previously been submitted to investigation. New experiments show that there are two continuous hydrogen spectra, one of which is situated in the ultra-violet at about λ 2500 and the other in the bluish-violet region. The emission phenomena in question are associated with the presence of positively charged ions in the gas, the bluish-violet spectrum being connected with the $H_2^{\cdot}$ ion and the ultra-violet with the $H^{\cdot}$ ion. The intensity of the two spectra is greatest under conditions in which combination between electrons and positive ions is of greatest frequency. The bluish-violet emission is accordingly of high intensity in the blue layer at the commencement of the

positive column, whilst the ultra-violet continuous spectrum is emitted in high intensity by the hydrogen canal rays.

Continuous spectra are also emitted by the vapours of the alkali and alkaline earth metals, cadmium, and mercury, and in these cases also the emission is dependent on the presence of positively charged metal ions. The frequency with which these ions combine with electrons determines the intensity of the continuous spectra, and these are accordingly emitted by the positive column in glow discharge through the vapour, and in the case of the alkali and alkaline earth metals by the Bunsen and oxyhydrogen flames in which the vapours are present.

It is suggested that all the elements will probably give rise to a continuous emission spectrum of the above-mentioned type under favourable conditions. According to the nature of the element, this spectrum may be situated in the visible, ultra-red, or ultra-violet region. H. M. D.

Spectroscopic Observations on the Active Modification of Nitrogen. V. Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 254—267).—The faint red bands λ 6394·45, λ 6468·53, λ 6544·81, and λ 6623·52 observed in the spectrum of the nitrogen afterglow have been further examined under conditions which preclude the possibility that they are to be attributed to the light of stray discharges in the observation tube. These bands, which belong to the α-group, are found in undiminished intensity when stray electric discharges are rigidly excluded, and are therefore characteristic of the afterglow spectrum.

The β- and γ-groups of bands appear in most cases with the same relative intensities, and it has been previously suggested that they are both due to oxides of nitrogen. The brightness of the visual afterglow (α-group) is enhanced in presence of small quantities of other substances which act as catalysts, and it is found that those substances which yield oxygen increase the intensity of the β-group, whilst catalysts which do not yield oxygen brighten up the visual afterglow, but have no influence on the intensity of the β- and γ-groups of bands. By subjecting the nitrogen used to the action of a concentrated alkaline solution of pyrogallol and of phosphoric oxide in order to remove oxygen, carbon dioxide, and water as far as possible, it has been found that the intensity of the β- and γ-groups of bands is greatly reduced. From experiments with nitrogen purified in this manner, it appears that the addition of oxygen or nitric oxide to the afterglow brings out the β- and γ-bands with a certain relative intensity. The addition of carbon dioxide gives greater relative intensity to the β-bands and carbon monoxide to the γ-bands. The addition of sufficient quantities of nitric oxide or nitrogen peroxide to the afterglow causes the β- and γ-groups to disappear, and a visually greenish, continuous spectrum is then obtained. The same spectrum, together with the γ-, but not the β-group, appears when nitric oxide is passed into a blow-pipe flame.

The introduction of oxygen into the afterglow is not accom-

panied by any measurable oxidation, and for this reason it does not seem possible to attribute the β- and γ-groups of bands to nitric oxide. H. M. D.

The *L*-Series of the Elements of High Atomic Weights. R. LEDOUX-LEBARD and A. DAUVILLIER (*Compt. rend.*, 1917, **164**, 687—690. Compare Moseley, A., 1914, ii, 14; and Barnes, A., 1915, ii, 658).—A study of the *L*-series of radiations in the cases of tungsten, iridium, platinum, and gold. The series comprises nine rays, which occur independently of the mode of generation of the electrons. The results verify the law $\nu = A(N - 7{\cdot}4)^2$, ν being the frequency, N the atomic number of the radiator, and A a constant. Plotting N against $\sqrt{\nu}$, all the rays of the series appear to lie on straight lines, but the homologous rays of the central part of the series are not similar in intensity. The intense rays for tungsten are numbers 4 and 6, and for iridium, platinum, and gold 4 and 5. W. G.

Quantitative Absorption Spectra. II. A New Ultra-violet Photometer. FREDERICK RUSSELL LANKSHEAR (*Mem. Manchester Phil. Soc.*, 1916, **60**, No. 10, 1—4. Compare A., 1915, ii, 605).—The photometer described is of the sector type, differing from previous instruments, however, in that the sector has a single semicircular aperture the diameter of which passes through the centre of the circular sector. By means of a disk with a corresponding aperture, which rotates on the face of the sector wheel, the aperture of the sector may be varied at will. H. M. D.

The Ultra-violet Transparency of certain Coloured Media. H. W. L. ABSALOM (*Phil. Mag.*, 1917, [vi], **33**, 450—455). —In the search for a substance opaque to the yellow region but transparent to the ultra-violet portion of the spectrum, the author has examined a number of coloured minerals and precious stones. Blue rock-salt from Stassfurt was found to transmit ultra-violet rays down to λ 2250, and the same degree of transparency was found for sylvite and for rock-salt and sylvite which had been coloured by the action of cathode rays.

Since the colour of blue rock-salt has been attributed to colloidal sodium, the investigation was extended to the blue solutions of metals in liquid ammonia. The most stable of these is the blue magnesium solution, which was found to transmit ultra-violet rays down to λ 2442. The limit of transmission for liquid ammonia is λ 2393.

These results would seem to show that ultra-violet transparency in a coloured mineral is favourable to the view that the colour is to be attributed to the presence of a colloidal metal. H. M. D.

Absorption of the Ultra-violet Rays by the Iodo-derivatives of Methane. G. MASSOL and A. FAUCON (*Compt. rend.*, 1917, **164**, 813—816).—Iodine in alcoholic solution shows three absorption bands, namely: (1) from $\lambda = 495$ to $\lambda = 420$ (max.

$\lambda = 470$—465); (2) from $\lambda = 389$ to $\lambda = 339$ (max. $\lambda = 355$); (3) from $\lambda = 300$ to $\lambda = 275$ (max. $\lambda = 288$—287). The four iodo-derivatives of methane show the selective absorptive properties of iodine, but considerably modified, so that each derivative shows a particular spectrum. The first band of free iodine is not shown by any of the four iodo-derivatives of methane. The second band is shown by carbon tetraiodide and iodoform, but considerably broadened in the direction of increasing values of λ and with its maximum slightly displaced. The third band is found with carbon tetraiodide and iodoform slightly broadened towards the shorter wave-lengths, and in the case of di-iodomethane it occurs as a band stretching from $\lambda = 330$ to $\lambda = 262$, with a maximum at $\lambda = 288$. With methyl iodide, a new band occurs at $\lambda = 270$ to $\lambda = 240$, having its maximum at $\lambda = 250$. W. G.

Spectrographic Investigations of Azole Derivatives. I. Pyrazole and its Derivatives. N. A. Rozanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1221—1250).—The author has investigated the absorption spectra of the following compounds: pyrazole, pyrazoline, 5-chloro-3-methylpyrazole, 3:5-dimethylpyrazole, 1:3:5-trimethylpyrazole, 3:4:5-trimethylpyrazole, 4-nitro-3:5-dimethylpyrazole, 1-phenylpyrazole, 3:5-diphenylpyrazole, 5-chloro-3-phenylpyrazole, 5-chloro-1-phenyl-3-methylpyrazole, 3-chloro-1-*o*-tolyl-5-methylpyrazole, 5-chloro-1-*o*-tolyl-3-methylpyrazole, 5-chloro-1-*o*-tolyl-3:4-dimethylpyrazole, pyrazolone, 3-methyl-5-pyrazolone, 3-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 3-chloro-1-phenyl-5-pyrazolone, 1-phenyl-3-methyl-5-pyrazolone, 1-*p*-tolyl-3-methyl-5-pyrazolone, 1-*o*–tolyl-3 : 4-dimethyl-5-pyrazolone, 1-phenyl-2 : 3-dimethyl-5-pyrazolone, 1-*o*-tolyl-3-methyl-5-pyrazolone, 3-hydroxy-1-phenyl-5-pyrazolone, 1-phenyl-5-methyl-3-pyrazolone, 1-*o*-tolyl-5-methyl-3-pyrazolone, 1-*p*-bromophenyl-5-methyl-3-pyrazolone, 1-*m*-nitrophenyl-5-methyl-3-pyrazolone, 4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone, glyoxaline, and thiazole. From the results obtained, which are expressed as both curves and tables, the following conclusions are drawn.

The slight absorption of an open, saturated chain is changed very little by closure of the ring, the degree of absorption of pentane and *cyclo*pentane being one and the same. Introduction of an unsaturated nitrogen atom, and consequently of a double linking into the ring, intensifies the absorption. Hexane and *cyclo*hexane show weak absorption, *cyclo*hexene and *cyclo*hexadiene increasing general absorption, and benzene pronounced selective absorption with seven absorption bands. If selective absorption is explained as due to certain vibrations of the chemical molecule about a position of equilibrium, these occurring readily only with compounds of unsaturated character with an odd number of unsaturated groups (compare Baly and Collie, T., 1905, **87**, 1332), the introduction into the benzene nucleus of a new unsaturated group, such as the element nitrogen, should cause weakening of the oscillations and simultaneous diminution of the selective absorption; this is actually found to be the case, pyridine exhibiting only

one absorption band. Contrary to expectation, introduction of a second nitrogen atom into the benzene nucleus does not enhance this effect, the intensity of the absorption bands with pyrazine being almost the same as with pyridine. It seems that, owing to the non-contiguity of the unsaturated elements, the vibrations of the molecule are not brought completely to a position of equilibrium, so that the selective absorption persists.

Confirmation of these relations is found with five-membered rings. Pyrrole exhibits greater absorption than *cyclo*pentane, and, as should be the case with a compound containing an odd number of unsaturated linkings, slight selective absorption. That introduction of a second nitrogen atom contiguous to the first into the pyrrole nucleus results in the annulment of the selective absorption is shown by the data for pyrazole and the simplest of its derivatives with saturated substituents. If, however, the second nitrogen atom introduced into the pyrrole is not adjacent to the first, the vibration should reappear, and, as is actually the case with glyoxaline, selective absorption be exhibited.

The results accompanying introduction of the unsaturated element sulphur into the glyoxaline molecule, and conversion of the latter into thiazole, which exhibits general absorption, are in contradiction to the above considerations, since, according to the latter, thiazole should exhibit selective absorption. Explanation of this point requires the investigation of a number of compounds of this type, including thiazole itself, of which the author had only a little at his disposal.

When the degree of unsaturation of pyrazole is diminished, as with pyrazoline, the extent of the absorption decreases. The unsaturated character of pyrazole compounds persists, however, on formation of salts, which give the same absorption curves as the corresponding bases, except for small alterations in the case of 5-chloro-3-phenylpyrazole. Introduction of auxochrome groups of the aliphatic series into the pyrazole nucleus results only in the displacement of the curves to the visible part of the spectrum, such displacement being most pronounced with the ortho-derivatives. If aromatic groups or the unsaturated nitro-group are inserted, absorption bands appear.

As regards oxygenated derivatives of pyrazole, pyrazolone gives an absorption band remaining constant on addition of alkali, so that only the ketonic grouping is to be attributed to it. If derivatives of pyrazolone do not give absorption bands, they must be regarded as derived from the iminic grouping of pyrazole. Hydroxy-derivatives of pyrazolone should react in two tautomeric forms, the ketonic and the enolic, and that this actually happens is shown by the alteration of the absorption curves on addition of alkali. Derivatives of 3-pyrazolone show curves very similar to that for 1-phenyl-2:3-dimethyl-5-pyrazolone (antipyrine), and should possess an iminic grouping, unalterable by alkali or acid; in general, these compounds absorb more strongly than the corresponding 5-pyrazolones.

The introduction of nitro-groups into the pyrazolone molecule

causes marked change in the absorption curve, this being connected with tautomeric transformation of the pyrazolonic grouping, since the compounds obtained are capable of salt formation, this being exhibited clearly in the case of picrolonic acid.

The auxochrome theory of colour is confirmed in the derivatives of pyrazole. The groups :N·NH·, ·N:CH·NH·, and ·S·CH:N· are markedly chromophoric, the cause of this lying in the unsaturated nature, not only of the nitrogen itself, but of the whole group in general, since otherwise the formation of salts would exert an influence on the spectrographic curves. T. H. P.

Optical Activity of Proteins, Enzymes, Toxins, and Serums. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1251—1294).—The author has collected from all sources data which have been obtained relative to the optical activity of animal and vegetable proteins and their derivatives, enzymes, toxins, and anti-serums. T. H. P.

Rate of Diffusion and Diameter of the Atom of Radium Emanation. Elisabeth Róna (*Zeitsch. physikal. Chem.*, 1917, **92**, 213—219).—The rate of diffusion of radium emanation in water, ethyl alcohol, benzene, and toluene is determined. From the diffusion constant D, the diameter S of the atom is calculated from the formula $S=RT/6\pi N\eta D$, in which N is the Avogadro constant $=6\cdot2\times10^{23}$ and η the viscosity of the solvent. The values thus obtained are 1·75, 0·63, 1·30, and $1\cdot24\times10^{-8}$ in water, ethyl alcohol, benzene, and toluene respectively. The differences between the several values are attributed to the lack of proportionality between the diffusion constant and the viscosity.

It is to be noted that the diffusion constants given by the author's measurements are very much larger than those previously obtained by Wallstabe (*Physikal. Zeitsch.*, 1903, **4**, 721). H. M. D.

Röntgen-investigation of Allotropic Forms. J. Olie, jun., and A. J. Byl (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 920—922).—According to Debye and Scherrer (*Physikal. Zeitsch.*, 1916, **17**, 277), secondary-ray interference figures are obtained when a finely divided, crystalline or quasi-amorphous substance in the form of a thin disk is subjected to the action of homogeneous X-rays. From the nature of the interference figure, conclusions may be drawn relative to the crystalline form of the substance in question.

The question of the behaviour of allotropic forms of the same substance has been examined by observations on the interference figures given by disks of compressed graphite and diamond powder. By the action of copper rays ($\lambda=1\cdot549\times10^{-8}$), interference figures of markedly different type were obtained with these two forms of carbon. H. M. D.

Kinetic Hypothesis to Explain the Function of Electrons in the Chemical Combination of Atoms. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1917, **39**, 879—882).—A theoretical paper in which a brief review is given of the views held from the time of Berzelius down to the present day, of the connexion between electricity and matter. On the basis of the two generally held assumptions, the author puts forward an hypothesis to explain the function of the electron in chemical combination. On the assumptions (1) that the atoms are of a complex structure made up of positive nuclei and electrons, of which the latter are in rapid motion and have a velocity of about sixty times that of the hydrogen molecule, and (2) that the electrons are of two kinds in their relation to the structure of the atom, some of them being so involved in their orbits among the positive nuclei that they can never escape from the atom, and others, valency electrons, being transferable to other atoms, the author explains chemical combination in the following way. When two atoms, *A* and *B*, which have affinity for one another are brought together, a valency electron rotating round a positive nucleus in *A* may find a positive nucleus in *B* sufficiently close to include the latter in its orbit, and it may then continue to describe an orbit about both positive nuclei. During that portion of the orbit within *B*, *B* would become, on the whole, negative, whilst *A* would be positive. During the other part of the orbit, each atom would be electrically neutral, and the atoms might fall apart. Remembering the rapidity of the motion of the electron when compared with that of the atom, it appears that the motion of an electron in such an orbit might hold two atoms together. In ionisation, the electron would rotate about the nucleus of the negative atom, leaving the other atom positive. This hypothesis may be used to account for the localisation of the affinities in particular parts of the atoms, which is indicated by many organic compounds. J. F. S.

Electrical Conductivities of Dilute Sodium, Potassium, and Lithium Amalgams. THOMAS B. HINE (*J. Amer. Chem. Soc.*, 1917, **39**, 882—895).—With the object of gaining an insight into the mechanism of the electrical conduction of metals, the author has determined the resistance of dilute amalgams of sodium, potassium, and lithium. The dilute amalgams were prepared from a concentrated amalgam of known composition in each case by adding measured volumes of mercury to it. The concentrated amalgams were prepared by the electrolysis of the alkali carbonates, using a pure mercury cathode. In the case of sodium, eleven different amalgams were measured, varying from 0·9 to 4·9 atoms %. The addition of sodium to mercury up to 2·40 atoms % increased the resistance, after which the value decreases again, and at 4·916 atoms % has practically reached the original mercury value. Seven determinations were made with lithium amalgams containing from 0·03 to 0·82 atom %; in this case the resistance decreases continuously with the addition of lithium. Seven determinations were also made with potassium amalgam containing from 0·058 to 1·186

atoms %. The resistance increases continuously with the addition of potassium. These results are considered from the point of view of the electron theory of conduction, and it is shown that the mechanism of conduction in the case of these amalgams is more complicated than that presented by the drift of free electrons due to an *E.M.F.* superimposed upon their disordered thermal motion.

J. F. S.

Conductivity Measurements on Oxidation-reduction Reactions. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1917, **39**, 914—928).—Conductivity measurements have been made of solutions of ferrous sulphate which is being oxidised by the addition of potassium dichromate solution, and of potassium dichromate which is being reduced by the addition of ferrous sulphate. The measurements were made both in the presence of hydrochloric acid and sulphuric acid. In all cases reaction–conductivity curves are given, and the end-point of the reaction ascertained. In the oxidation of ferrous sulphate, it is shown that the curves are of the same general type as is observed in the neutralisation of an acid by a weak base, or of a base by a weak acid. The conductivity drops during the progress of the reaction, and then changes very little with an excess of dichromate. The conductivity may rise slightly, fall slightly, or remain constant after the end-point has been passed, depending on the acidity of the solution. The reason for the drop in the conductivity during the progress of the reaction is given by the equation

$$6Fe^{++} + Cr_2O_7^{=} + 14H^{+} = 6Fe^{+++} + 2Cr^{+++} + 7H_2O.$$

The concentration of the hydrogen ion falls during the reaction, and since the hydrogen ion in these strongly acid solutions carries most of the current, the conductivity must fall with it. After the end-point is reached, further addition of dichromate causes little change in the conductivity. The curves both before and after the end-point is reached are linear within the limits of experimental error. In the reverse action, that is, the reduction of potassium dichromate, the shape of the curve differs with different experimental conditions. If an acidified solution of potassium dichromate is titrated with ferrous sulphate to which no acid has been added, the curves are identical with those already described, but if to the ferrous sulphate such a quantity of acid has been added to make the solution of the same normality, both with regard to acid and ferrous iron, then the curve drops very slowly to the end-point and then rises steeply. A few preliminary results are given of the conductivity of ferrous sulphate solution which is being oxidised by potassium permanganate. On the whole, the conductivity reaction curves are the same as those obtained for dichromate, although the slope is not quite so great in this case. In these determinations, the permanganate must be added very slowly, particularly towards the end of the reaction. The influence of a number of factors on the conductivity reaction curves is discussed.

J. F. S.

Electrical Conductivity of Several Salts in Pyridine. J. HOWARD MATHEWS and ALFRED J. JOHNSON (*J. Physical Chem.*, 1917, **21**, 294—310).—The electrical conductivity of lead nitrate, silver sulphate, copper acetate, silver thiocyanate, silver cyanide, and silver chloride has been determined at 25°, and in the first two cases at 0°, in pyridine solutions over a long range of concentration. The authors show that electrolytes fall into four classes: (1) those for which the equivalent conductivity curve rises rapidly in the more concentrated solutions and becomes asymptotic in the more dilute solutions; (2) those for which the conductivity increases more rapidly in the dilute solutions; (3) those which give minimum values for the equivalent conductivity; and (4) those which show an irregularity in their equivalent conductivity curves. The curves for silver sulphate, copper acetate, silver thiocyanate, and lead nitrate show an increase in the conductivity with increasing dilution without any indication of a maximum value being apparent. The curves for silver cyanide become almost parallel with the volume axis at intermediate dilutions, whilst silver chloride exhibits the same type of curve in a less marked degree. A résumé of the more recent hypotheses put forward to explain the anomalies found in electrical conductivity of salts in pyridine solution is given, and these hypotheses are discussed in the paper. J. F. S.

Potential of the Hydrogen Electrode at Different Pressures. N. E. LOOMIS, C. N. MYERS, and S. F. ACREE (*J. Physical Chem.*, 1917, **21**, 334—337).—The authors have undertaken the investigation of the hydrogen potential under different pressure conditions; in the present note they detail the various factors which have to be taken into account in the work. J. F. S.

Electromotive Forces and Electrode Potentials in Pure and Mixed Solvents. II. F. S. MORTIMER and J. N. PEARCE (*J. Physical Chem.*, 1917, **21**, 275—293. Compare A., 1915, ii, 7). —The electrode potentials $Ag|Ag^{\cdot}$ have been determined at 0° and 25° for solutions of silver nitrate in water, methyl alcohol, ethyl alcohol, pyridine, and binary mixtures of these solvents at a series of different concentrations. The dielectric constant has also been determined for the pure and mixed solvents. It is shown that the electrode potentials of silver are much higher for solutions in water and the two alcohols than for equivalent concentrations in pyridine. For any given concentration of silver nitrate, the *E.P.* increases with the decrease in the amount of pyridine present in the solvent. This increase is very gradual until 75% of the pyridine has been replaced by the second solvent. In the case of mixtures of pyridine with water or methyl alcohol, the dielectric constant increases, at first rather slowly with decrease in the percentage of pyridine, and then more rapidly with further decrease in the pyridine content. In all solvents, pure or mixed, the *E.P.* values increase with increasing concentration of the salt. The *E.M.F.* of all possible concentration cells in each of the

pure and mixed solvents has been determined, and the values determined are shown to agree with those calculated from the *E.M.F.* values of solutions in the pure solvents in the case of water and the two alcohols; in the case of pyridine, however, the values calculated for the concentration cells from conductivity data do not even approximately agree with the experimentally determined *E.M.F.* values. Hence it is concluded that either the Nernst equation does not hold for concentration cells in pyridine or the electrical conductivity of these solutions is in no sense a measure of the degree of ionisation. The following values of the solution pressure of silver have been calculated from the experimental data: water, $2{\cdot}46 \times 10^{-17}$ atms.; ethyl alcohol, $2{\cdot}02 \times 10^{-18}$ atms.; methyl alcohol, $3{\cdot}55 \times 10^{-19}$ atms.; and pyridine, $1{\cdot}77 \times 10^{-10}$ atms. The heat of ionisation is calculated in the case of all solutions; for the pure solvents the following values are obtained: in water, 23,728 cal.; in pyridine, 3726 cal.; in ethyl alcohol, 21,472 cal.; and in methyl alcohol, 22,400 cal. The following dielectric constants have been obtained: water, 80·5; 75% water, 25% pyridine, 56·9; 50% water, 50% pyridine, 41·1; 25% water, 75% pyridine, 31·5; pyridine, 11·2; methyl alcohol, 32·8; 75% methyl alcohol, 25% pyridine, 24·5; 50% methyl alcohol, 50% pyridine, 18·2.

J. F. S.

The Theory of Overvoltage. EDGAR NEWBERY (*Mem. Manchester Phil. Soc.*, 1916, **60**, No. 11, 1—34. Compare T., 1914, **105**, 2434; 1916, **109**, 1051, 1066, 1107).—An account is given of the phenomena of overvoltage, the factors on which it depends, the methods of measuring the effect, and the theories which have been put forward to account for overvoltage.

None of these theories is in agreement with all the facts at present known, and a new theory is suggested which includes certain ideas involved in the older theories of Nernst, Le Blanc, and Foerster. According to this, the overvoltage effect at the surface of a metal is determined by four factors, defined as (1) supersaturation of the metal surface with gas in consequence of the permeability of the metal to the ionised gas and its impermeability to non-electrified gas molecules, and, further, of the spontaneous decomposition of the alloys which are formed by the metal and the gas in question; (2) formation of alloys or solid solutions at the electrode surface; (3) relative concentration of non-hydrated ions, charged and discharged, at the metal surface; (4) inductive action of the escaping ionised gas on the electrode. H. M. D.

[**The Passive Condition of Metals.**] J. STAPENHORST (*Zeitsch. physikal. Chem.*, 1917, **92**, 238—254).—In explanation of the relation between the active and passive states of a metal, it has been suggested that hydrogen and oxygen act as catalysts in promoting the transformation of one form of the metal into the other. A number of experiments are described in which the author seeks to distinguish between the hydrogen and oxygen theories as applicable to certain metals which show the phenomenon in question.

Iron which has been rendered passive by the action of chromic acid becomes active under the influence of hydrogen dissolved in the metal. In this experiment, the hydrogen was generated electrolytically on the opposite side of a thin iron plate, the hydrogen diffusing through the plate to the surface in contact with the chromic acid solution. It is shown that this change cannot be explained by the removal of dissolved oxygen or by the destruction of an oxide film. Under suitable conditions, the reverse change may be brought about by the diffusion of nascent oxygen.

The potential assumed by a metal in a neutral electrolyte depends on the quantity of oxygen present in the electrolyte solution. If the surface of the metal is renewed by grinding with an emery-wheel, the potential changes from that characteristic of the passive form to the value peculiar to the active form of the metal. Hydrogen and nitrogen tend to preserve the potential of the active form, but otherwise behave as indifferent gases. Oxygen, on the other hand, is not an indifferent gas. Both in the gaseous and dissolved states it exercises a very considerable influence on the electrode potential and conduces to the appearance and maintenance of the passive condition. H. M. D.

The Concentration of the Electrolytes in the Neighbourhood of the Electrodes. ST. PROCOPIU (*Compt. rend.*, 1917, **164**, 725—727).—It has previously been shown that in addition to the Helmholtz-Lippmann double layer round the electrode, there is another layer of electrolyte of concentration different from that of the mass of liquid (compare A., 1915, ii, 816). A formula is now given for determining the thickness of this layer, namely, $x_1 = x_0 e^{kv/v}$, where x_1 is the thickness of this layer, x_0 is the thickness of the double layer, k the dielectric constant of the solvent, v the *E.M.F.* produced by displacement of the electrode, and v is the potential, metal–liquid. A comparative idea of the thickness of this second layer is obtained by determining how soon the *E.M.F.*, produced by the movement of the electrode, disappears. W. G.

Examples of Electrolysis with Alternating Current. A. RÍUS Y MIRÓ (*Anal. Fis. Quim.*, 1917, **15**, 182—191).—An account of electrolyses carried out with alternating currents of different frequencies in dilute solutions of sulphuric acid, hydrochloric acid, and sodium hydroxide, electrodes of copper, iron, and aluminium being employed. A. J. W.

The Electro-capillary Function. G. GOUY (*Ann. Physique*, 1917, [ix], **7**, 129—184).—A theoretical discussion of results previously published (compare A., 1906, ii, 652, 725; 1908, ii, 654; 1916, ii, 550). W. G.

The Cooling of Different Metals by Immersion in Water. GARVIN and A. PORTEVIN (*Compt. rend.*, 1917, **164**, 783—786).—A study of the cooling curves of silver, aluminium, nickel, and a

nickel-steel containing 30% of nickel, the metals being used in the form of homothetic cylinders, the diameter varying between 8 mm. and 20 mm. and the length equal to 3*d*., the metals being tempered in a current of water at high temperatures. The work was carried out under the conditions formulated by Le Chatelier (compare *Rev. de Métallurgie*, 1904, **1**, 475) and realised by Benedicks (compare *J. Iron Steel Inst.*, 1908, 153). The results and curves, which will be published in another communication, show that concordant curves are obtained for the samples which cool slowly, but for the others considerable variation is found. The curves show a point of inflexion corresponding with the commencement of tempering. Beyond this point the curves do not appear to obey a mathematical law, as suggested by MacCance (compare *J. Iron Steel Inst.*, 1914, **89**, 192). The velocity of cooling increases slightly when the temperature of tempering is raised.

W. G.

Cooling Curves of Ternary and Quaternary Mixtures. N. PARRAVANO and C. MAZZETTI (*Gazzetta*, 1917, **47**, i, 133—143).—Cooling curves of mixtures often fail to present distinctly the discontinuities which are characteristic of them, and are utilised for constructing diagrams of state. Of the various causes contributing to this failure, the form of the melting-point diagram of the series to which a mixture belongs and the position of the mixture in this series have been insufficiently considered. Hanemann (A., 1915, ii, 413) has, however, shown that, with binary mixtures it is possible generally to establish the influence exerted on the form assumed by the cooling curves by the form of the diagram and the position of the mixture in it. The authors now indicate, with the help of figures, how the form which may be expected for the cooling curves of ternary and quaternary mixtures may be established when the diagram of state is known; in some cases the deductions usually drawn from the discontinuities observed in the cooling curves are found to be inaccurate.

T. H. P.

A Statistical Study of Organic Series. W. E. FORBES (*Chem. News*, 1917, **115**, 229).—By comparing the so-called coefficients of variation of the boiling point for various homologous series it is found that the value for the paraffin hydrocarbons is much greater than the values for the alcohols, fatty acids, and the benzene series of hydrocarbons. The difference shown by the paraffin and the benzene series of hydrocarbons is supposed to be connected with the structure of the benzene nucleus. H. M. D.

Heat of Formation of Ferrous Sulphide. N. PARRAVANO and P. DE CESARIS (*Gazzetta*, 1917, **47**, i, 144—149).—The authors have determined the heat of formation of ferrous sulphide calorimetrically, the reaction between finely divided reduced iron and sulphur being initiated by a platinum wire electrically heated. The number of cals. generated per 1 gram of ferrous sulphide

varied from 258·2 to 266·0, the mean being 262·4 and the molecular heat 23,070 cals. For the precipitated sulphide, Berthelot found 24,000 and Thomsen 23,780 cals.

Neglecting the small thermal change accompanying the polymorphic transformation of ferrous sulphide at 298°, the dissociation pressures for ferrous sulphide and manganese sulphide are calculated from the Nernst formula, $\log p = -Q/4{\cdot}571T + 1{\cdot}75 \log T + 3$, for the temperatures 800°, 900°, 1000°, and 1100°, the values for the latter being much smaller than those for the former at the same temperature. Consequently, the reaction $FeS + Mn = MnS + Fe$ should take place, as is indeed known to be the case. T. H. P.

Molecular Condition of Pure Liquids. II. P. N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1175—1196. Compare this vol., ii, 125).—The considerations previously developed show that Kistiakovski's rule (A., 1906, ii, 655; 1913, ii, 837) is quite inapplicable to the investigation of the molecular constitution of liquids.

A number of further conclusions are deduced, the principal ones being as follows. The molecular volumes of normal liquids at corresponding temperatures (in corresponding states) are equal. Equal volumes of normal liquids at identical reduced temperatures and pressures contain equal numbers of molecules. Further, normal liquids and their saturated vapours under corresponding conditions possess those structural peculiarities which Avogadro discovered for gases (ideal) at identical absolute temperatures and pressures. The true molecular volumes of all liquids (normal and abnormal) at corresponding temperatures and under the pressure of their saturated vapours are equal.

The ratio, $V_1 : V$, of the molecular volume of an abnormal liquid to that of a normal liquid at the corresponding temperature is termed the abnormality number, N, and abnormal liquids are associated or dissociated according as N is less than or greater than unity. In investigating the molecular volumes of liquids, these are compared with the values for carbon tetrachloride at the corresponding temperatures, and use is made of functions of the form $\gamma v^n/T$ or of some other function containing γ.

The values of N have been calculated, and are tabulated, for 108 elements and compounds, of which only four, namely, carbon tetrachloride, ether, ethyl acetate, and propyl formate, exhibit normal molecular volumes. The data for homologous series show that the accumulation of mass in a molecule diminishes the association and increases the dissociation of liquids. Thus, methane is strongly associated, *n*-pentane dissociated, *n*-hexane more dissociated, and *n*-heptane still more dissociated. Further, benzene is associated, toluene dissociated, xylene more dissociated, and mesitylene and durene still more dissociated. A similar relation holds for the series water, methyl, ethyl, propyl, butyl, and *iso*amyl alcohols, for the series of carboxylic acids, esters, etc., and for such series as benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. Marked association is exhibited by the elements in the liquid condition. T. H. P.

Comparative Adsorption of Sucrose, Inulin, and Dextrin. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1319—1324).—The author's previous work indicates that the necessary conditions for every adsorption include the colloidal state of the adsorbed substance and adsorbent, the only case observed in which a crystalline substance is irreversibly adsorbed by a colloidal adsorbent being that of the solid paraffins of naphtha by aluminium hydroxide, floridin, etc.

In order to test the accuracy of Freundlich's rule, that adsorption is prevented by a tendency to dissociation and by an accumulation of hydroxyl groups, the author has now carried out experiments on the adsorption of sucrose, inulin, and dextrin. The results show that this rule holds only for crystalline carbohydrates, such as sucrose and inulin; colloidal carbohydrates, on the other hand, are well adsorbed by both aluminium hydroxide and animal charcoal, and in the case of dextrin (commercial "dextrinum purissimum") both these adsorptions are irreversible with respect to boiling water. Further, both adsorptions are quantitative; animal charcoal adsorbs 8·04% of β-achroodextrin and aluminium hydroxide 16·02% of products intermediate to β- and γ-dextrins. The above commercial dextrin is found to be a mixture of maltodextrin with β-achroodextrin and products intermediate to β- and γ-achroodextrins. T. H. P.

The Osmotic-Kinetic Theory of Dilute Solutions. KARL JELLINEK (*Zeitsch. physikal. Chem.*, 1917, **92**, 169—212).—A theoretical paper in which the osmotic theory of solutions is examined from the kinetic point of view. It is shown that the van der Waals's equation may be employed in the derivation of the relation between the osmotic pressure, the concentration, and the temperature and of the laws regulating the lowering of the vapour pressure and the freezing point and the raising of the boiling point. The assumptions made in the theoretical treatment are (1) additivity of the volumes of solvent and solute, (2) additivity of the volume correction factor b. H. M. D.

Calculation of the Coefficient of Diffusion of a Salt at a Definite Concentration. A. GRIFFITHS (*Proc. Physical Soc.*, 1917, **29**, 159—162).—It is shown that the coefficient of diffusion may be calculated without a knowledge of the exact relation between the density and the concentration of the solution. The method of calculation adopted by Clack (compare A., 1915, ii, 45) is thereby justified. H. M. D.

Osmotic Pressure: its Relation to the Membrane, the Solvent, and the Solute. FRANK TINKER (*Phil. Mag.*, 1917, [vi], **33**, 428—450).—A theoretical paper in which the author discusses the relation of osmotic pressure to the solvent, the solution, and the semipermeable membrane. It is assumed that the pressure of each component in the interior of a fluid mixture is inversely propor-

tional to the free space available to the molecules, and that the exact relation between the partial pressure of the component and the free space per molecule is given by the equation–partial pressure × available free space per molecule of the component $=RT$. Dissociation and association of the solute and solvent and combination between them are also supposed to be excluded.

By making use of the Dieterici equation of state it is shown that two ideal solutions of equal molar concentration are in osmotic equilibrium, that this equilibrium does not obtain if one solution is ideal and the other not, although the solutions may be equally concentrated, and that osmotic equilibrium between non-ideal solutions is possible only when the solutions have equal heats of dilution.

The general equation connecting the osmotic pressure with the vapour pressures of solvent and solution, both supposed to be at atmospheric pressure, reduces for dilute solutions to the form $PV=RT+q$, in which V is the volume of solution containing 1 mol. of solute and q is a measure of the heat change on dilution. This equation has already been given by Bancroft (A., 1906, ii, 523). It follows that the osmotic pressure of a dilute solution is given by the simple gas equation only when the solution has zero heat of dilution. If the heat of dilution is positive, the osmotic pressure is abnormally high, whilst if the heat of dilution is negative the osmotic pressure is abnormally low.

Consideration of the compressibility relationships shows that the free space within a dilute solution having zero heat of dilution is equal to $RT\beta$, where β is the coefficient of compressibility. Since the pure solvent is the limiting case of a dilute solution, this relation must hold for pure liquids. H. M. D.

Pervaporation, Perstillation, and Percrystallisation. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1917, **39**, 944—948). —Collodion and parchment membrane containers permit water to evaporate through the walls as though no membrane were present. This phenomenon is termed pervaporation. Distillation by means of pervaporation is termed perstillation, and can be carried out at ordinary pressures with low temperatures, as well as in a vacuum. When a dialysable constituent of a liquid within these containers reaches saturation, crystallisation usually takes place on the outside of the container; this is termed percrystallisation. A number of experiments are described to show the nature of these phenomena; thus it is shown that in twenty-four hours 325 c.c. of a solution containing serum albumin and 25 c.c. of toluene had lost all its water at 37° when closed in a collodion container. Also pervaporation occurs so rapidly when water is placed in a closed collodion vessel and heated by a Bunsen flame that the liquid sinks in the vessel perceptibly, like a slowly emptying burette. It is also shown that it is not possible to raise the temperature of water in such a container above 92° when a Bunsen is used as the source of heat. The cause of these phenomena is discussed and tentative hypotheses are put forward to explain them. J. F. S.

Crystal Structure and Chemical Valency. J. Beckenkamp (*Centr. Min.*, 1917, 97—110).—If the Sohncke theory of point systems be rigidly applied to crystals, the conceptions of molecule and valency in such structures become meaningless. In the structures put forward by W. H. and W. L. Bragg for rock-salt and sylvine, the atoms of the two kinds form an interpenetrating point system, and no molecules are distinguishable. The author shows that in the structures which he has already put forward for various minerals, for example, for quartz, the individuality of the molecule is preserved. The author supposes the distances between atoms in the structure to be determined by the positions of nodes formed by the interference of radiation waves from the respective atoms, the wave-lengths being a function of the atomic weights. He concludes, from the relative atomic weights of sodium and chlorine, that the ultimate structure of a crystal of rock-salt has a triclinic character, but that by a species of submicroscopic twinning a pseudo-regular structure is built up indistinguishable from a truly cubic one. The Bragg structure gives merely the average position of the atoms.

A similar conclusion has been reached by J. Stark (*Jahrb. Radioaktiv. Elektronik*, 1915, **12**, 280) from considerations of electro-affinity. He considers it impossible that intramolecular linkings can be destroyed in the crystal, but finds that in a structure of sodium and chlorine ions (rock-salt) there will be formed complexes having an axis of hemimorphous tetragonal symmetry. By the twinning of such complexes, a quasi-homogeneous mass having holohedral cubic symmetry results. E. H. R.

Results of Crystal Analysis. IV. The Structure of Ammonium Iodide, Tetramethylammonium Iodide, and Xenotime. L. Vegard (*Phil. Mag.*, 1917, [vi], **33**, 395—428. Compare A., 1916, ii, 405, 593).—The results obtained in the *X*-ray spectroscopic examination of crystals of ammonium and tetramethylammonium iodides indicate that the existence of a simple relation between the topic parameters does not necessarily involve any very simple relation between the lattices. It is shown that the morphotropic relationship cannot be explained by replacement of the hydrogen atoms in ammonium iodide by tetragonally arranged carbon atoms. The observations show, in fact, that the iodine and nitrogen lattices are not only quite differently arranged, but that the elementary lattice of tetramethylammonium iodide contains two molecules, whilst that of ammonium iodide contains four molecules.

Further investigation of the structure of xenotime has shown that the atoms of xenotime are arranged in a lattice of the zircon type, and the previously expressed opinion (compare *loc. cit.*) that the lattice systems are of different type can no longer be maintained. The conception of xenotime as a phosphate, YPO_4, is accordingly not in accordance with the crystalline structure, which suggests that the constitution of the substance in the crystalline form is that represented by YO_2PO_2. H. M. D.

Mixed Crystals. CARLO VIOLA (*Atti. R. Accad. Lincei*, 1917, [v], **26**, i, 195—207. Compare this vol., ii, 79, 80).—The author now proceeds to examine the equilibrium contact conditions between a mixed crystal and the amorphous phase from which it originates. This problem is solvable by means of the data required to prove Curie's law, according to which the growths perpendicular to the faces of a crystal are directly proportional to their respective capillary constants.

The mixed crystal is composed of two constituents, that is, of two crystals in intimate contact in their smallest parts. It will be in equilibrium with the amorphous phase, which contains the same constituents, but usually in different proportions, when (1) the proportion between the two components does not alter, although the total mass changes in correspondence with Gibbs's phase rule, (2) when the surface energy is a minimum in correspondence with the least action, and (3) when the total volume of the mixed crystal does not vary, the only possible variation being in the form.

It is shown analytically that the mean growths perpendicular to the faces of the mixed crystal are directly proportional to the mean capillary constants of the two components. From this it follows that the normal figure of a mixed crystal is the mean of the normal figures of the crystals composing it in the proportions in which these are found in the mixed crystal. It is shown further that the total surface energy is always directly proportional to the total volume of the mixed crystal, this being Curie's law, and that the difference in the surface energies of the components is directly proportional to the difference in the volumes at every instant of the growth, no matter what the relation between the components of the mixed crystal. Isomorphous crystals are defined as those having the same structure and the same surface density, and therefore exhibiting continuous miscibility between limits which include the mean miscibility. Various examples are considered in order to illustrate the significance of the inclusion in the above definition of the idea of mean miscibility.

T. H. P.

Mathematical Theory of the Kinetics of the Coagulation of Colloidal Solutions. M. VON SMOLUCHOWSKI (*Zeitsch. physikal. Chem.*, 1917, **92**, 129—168).—Inductive methods applied to the available data on the kinetics of coagulation processes have not led to any satisfactory theory of the coagulation process, and this is largely attributed to the circumstance that the properties of the colloidal solutions which have been investigated in this connexion do not afford a satisfactory indication of the progress of the coagulation.

An attempt is made to build up a theory of the phenomenon by deductive methods. It is assumed that the colloidal particles attract one another in virtue of capillary forces when the distance between them is sufficiently small. That this attraction does not lead to combination in normal circumstances is due to the pro-

tective action of the electrical double layer surrounding the particles. On the addition of an electrolyte, ion adsorption occurs and the double layer is partly or completely eliminated, with the result that the colloidal particles combine to form larger aggregates under the influence of the capillary forces. The Brownian motion of the particles only comes into play as a factor in coagulation in so far as it facilitates the approximation of the particles, and thus indirectly affects the operation of the capillary and electric forces.

Formulæ are derived for the course of an ideal coagulation which are found to be in satisfactory agreement with previous observations on the kinetics of coagulation processes. In regard to the influence of the concentration of the colloid on the rate of coagulation, these formulæ are comparable with equations for ordinary chemical reactions of the second order.

Rapid coagulation processes and chemical reactions may be regarded as opposite and extreme cases of the ideal coagulation processes which are more particularly considered in connexion with the author's theory. Whilst the former can be regarded as determined solely by diffusion factors, it would seem that ordinary chemical reactions involve some unknown factor, the effect of which is to reduce the number of collisions which result in chemical interchange to a very small fraction of the total number of the molecular collisions. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 2. Colloidal Silver. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 123—127. Compare this vol., ii, 244). —The preparation of colloidal solutions of silver by the action of sodium hyposulphite in presence of extract of *Tubera Salep* as protective colloid is described in detail. The silver sols thus obtained are of great stability, and this stability does not seem to be affected by the fact that the colour of the solutions in transmitted light varies with the conditions. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 3. Colloidal Arsenic. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 186—194).—Experiments are described in which the authors have examined the protective action of extracts of various plant colloids on colloidal arsenic prepared by the reducing action of sodium hyposulphite on slightly acidified solutions of arsenious oxide. The protective action is very marked, and it has been found possible to obtain by evaporation solid colloids containing about 3% of arsenic which are completely soluble in water.

According to observations on the colour, the protected solutions of colloidal arsenic are not appreciably influenced by the addition of hydrochloric acid, sulphuric acid, sodium chloride, and barium chloride, whereas sodium hydroxide and sodium carbonate change the colour from dark brown to light yellow. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 4. Colloidal Antimony. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 194—198).—Colloidal solutions of antimony, prepared by the action of sodium hyposulphite on a solution of potassium antimoniate acidified slightly by the addition of tartaric acid, are found to have their stability considerably increased in presence of the extract of *Tubera Salep*. The dialysed solutions may be evaporated to give solid colloids containing about 10% of antimony which dissolve completely in water. The stability of the protected solutions is not affected by the addition of acids and neutral salts, but alkalinity reduces the stability to a large extent. In this respect, the behaviour of the colloidal antimony solutions resembles that of solutions of the protective colloid. H. M. D.

The Use of Citarin in Scientific Chemistry. L. VANINO (*Kolloid Zeitsch.*, 1917, **20**, 122).—The addition of small quantities of the sodium salt of anhydromethylenecitric acid ("citarin") to solutions of gold, silver, and other metallic salts results in the formation of colloidal solutions of the respective metals. The colloidal gold solutions are red in colour, although violet-blue solutions are usually obtained by the action of other reducing agents. H. M. D.

Theory of Emulsification based on Pharmaceutical Practice. LEO ROON and RALPH E. OESPER (*J. Ind. Eng. Chem.*, 1917, **9**, 156—161).—The authors review briefly the theories of emulsification which have been advanced, and the methods employed in pharmaceutical practice for the preparation of emulsions. The present work was confined to the study of acacia and soap emulsions, and reveals the existence of definite critical points of emulsification, depending on the quantities of internal phase and of emulsifier, the nature of these two factors, and the procedure followed in the preparation of the emulsion. The results, in agreement with Fischer's theory, indicate that the presence of a hydration compound of the nature of a hydrated colloid is necessary for emulsification, and that the best emulsion is produced when this hydration compound is formed at the moment of dispersion of the internal phase; in other words, emulsifier, water, and oil in critical proportions must all be mixed together at once in order to form a properly hydrated nucleus, which may then be diluted. This is in accord with the usual pharmaceutical practice. No emulsion results if the emulsifier (gum acacia or soap) is diluted before the dispersion of the internal phase. Emulsion nuclei of one composition act as stabilisers or emulsifiers respectively for incomplete emulsions of other compositions, or for other internal phases. G. F. M.

In-, Uni-, and Bi-variant Equilibria. XIV. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 927—932. Compare this vol., ii, 195).—A discussion of the relations exhibited by systems in which three indifferent phases co-exist. H. M. D.

Equilibrium in the System: Mercuric Iodide-Pyridine. J. HOWARD MATHEWS and PHILIP A. RITTER (*J. Physical Chem.*, 1917, **21**, 269—274).—The solubility of mercuric iodide has been determined in pyridine at temperatures between $-50°$ and $+98·5°$. Over this range of temperature the solubility changes regularly from 1·95% mercuric iodide in the solution to 65·30%. It is shown that the saturated solution at all temperatures is in equilibrium with the compound $HgI_2,2C_5H_5N$, and this is the only compound which exists between these limits. It crystallises, however, either in long, monoclinic needles or in short, monoclinic prisms, but there appears to be no definite transition point between the two forms.

J. F. S.

Velocity of Reaction in Heterogeneous Systems and Size of Granules. EMIL PODSZUS (*Zeitsch. physikal. Chem.*, 1917 **92**, 227—237).—It has been found that certain oxides, which in ordinary circumstances are unacted on by hydrochloric acid, are dissolved by this reagent to a very appreciable extent when the oxides are reduced to a fine state of subdivision. The experiments were made with aluminium oxide, thorium oxide, and zirconium oxide, and in each case the oxide is dissolved when the diameter of the particles is of the order 1 μ. The results recorded show the progress of the dissolution when the concentration of the acid and the temperature are kept constant, and, further, the influence of variation in the acid concentration. It would seem that oxides which are apparently insoluble in acids may be dissolved provided the size of the particles is sufficiently reduced.

The observations cannot be explained in terms of the diffusion theory, and in consideration of the small size of the particles it is not surprising that the behaviour should deviate from that which has been found associated with reactions in heterogeneous systems. Although the size of the particles of a substance is known to have a considerable influence on many of its properties, including the solubility, it does not seem possible to account for the observed facts on this basis. H. M. D.

The Influence of Pressure on the Ignition of a Mixture of Methane and Air by the Impulsive Electrical Discharge. RICHARD VERNON WHEELER (T., 1917, **111**, 411—413. Compare *ibid.*, 130).—Further experiments on the influence of pressure on the energy of the igniting current have been made at pressures greater than atmospheric. No evidence of "stepped ignition" is shown by the results obtained at pressures varying from 500 to 5000 mm., the curve obtained by plotting the igniting current against the pressure of the gaseous mixture being perfectly continuous.

When a spark-gap of 1 mm. was employed at pressures somewhat higher than atmospheric, it was found that the least discharge which could cross the gap caused ignition of the mixture. By using a smaller spark gap (0·25—0·5 mm.), however, it was possible to make the observations required. This factor offers a possible ex-

planation of the divergent results obtained by Thornton (compare A., 1914, ii, 834), the suggestion being that his data disclose merely the influence of the pressure on the facility with which the discharge passes across the spark gap. H. M. D.

Velocity of Decomposition and the Dissociation Constant of Nitrous Acid. PRAFULLA CHANDRA RÂY, MANIK LAL DEY, and JNANENDRA CHANDRA GHOSH (T., 1917, **111**, 413—417).—Solutions of nitrous acid are readily obtained by the interaction of equivalent solutions of barium nitrite and sulphuric acid. Measurements of the rate of decomposition of nitrous acid solutions show that the reaction proceeds in accordance with the equation for a unimolecular change, the velocity-coefficients at 0°, 21°, and 40° being 0·00014, 0·00022, and 0·00057 respectively. According to conductivity data, the ionisation constant of the acid at 0° is $6·0 \times 10^{-4}$.

The most concentrated solution of nitrous acid which could be obtained at 0° by the above method was 0·185*N*. H. M. D.

Reduction of Mercuric Compounds. G. A. LINHART and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1917, **39**, 948—950).—In previous papers Linhart has shown that the velocity of the reduction of mercuric chloride by phosphorous acid and by sodium formate follows the equation for a reaction of the second order, and not that of a reaction of the third order (A., 1913, ii, 490; 1915, ii, 91). In the present paper it is shown that the reduction of mercuric compounds may be represented as going first directly to mercury or some substance which behaves like mercury, and then, if conditions permit, to mercurous compounds. This manner of representation accounts for the fact that the reaction is bimolecular, so far as concerns the kinetics of the reaction, and it removes the necessity for specific explanations for each reducing agent.
J. F. S.

Studies on the Walden Inversion. V. The Kinetics and Dissociation Constant of α-Bromo-β-phenylpropionic Acid. GEORGE SENTER and GERALD HARGRAVE MARTIN (T., 1917, **111**, 447—457).—According to conductivity measurements at 25°, the ionisation constant of α-bromo-β-phenylpropionic acid is 0·00172. The limiting conductivity of the sodium salt is $\Lambda_{\infty} = 79·0$, from which the mobility of the anion is 28 and λ_{∞} for the acid 375.

The kinetics of the displacement of bromine by hydroxyl have been investigated according to methods described previously (compare T., 1915, **107**, 908; 1916, **109**, 690). Both the free bromo-substituted acid and its sodium salt give at 50° almost exclusively the corresponding hydroxy-acid, but in presence of sodium hydroxide this reaction is accompanied by the formation of a considerable proportion of cinnamic acid as a result of the elimination of hydrogen bromide from the bromophenylpropionic acid.

Comparison of the velocity-coefficients obtained in experiments with solutions containing (1) the free acid, (2) its sodium salt, (3) the free acid with the addition of nitric or benzenesulphonic

acid, shows that the reaction measured is the action of water on the $CH_2Ph\cdot CHBr\cdot CO_2'$ ion. The non-ionised acid reacts with water much less rapidly at 50°.

The temperature-coefficient of the reaction is probably the highest yet observed for a pseudo-unimolecular reaction, the velocity becoming 4·6 times as great when the temperature is increased by 10°.

When the data for α-bromo-β-phenylpropionic acid are compared with results obtained for α-bromopropionic acid, it is found that the bromine is acted on less rapidly in the first-mentioned acid. This is not in accord with previous observations relative to the influence of the phenyl group in such reactions. H. M. D.

A New Method for the Measurement of the Velocity of Crystallisation of the Metals. J. Czochralski (*Zeitsch. physikal. Chem.*, 1917, **92**, 219—221).—The method depends on the determination of the maximum velocity with which a thin, crystalline thread of the metal may be drawn continuously from a bath of the liquid metal. The maximum velocities found for tin, lead, and zinc at their respective melting points were respectively about 90, 140, and 100 millimetres per minute. H. M. D.

Studies in Catalysis. VI. The Mutual Influence of Two Reactions proceeding in the same Medium. Robert Owen Griffith, Alfred Lamble, and William Cudmore McCullagh Lewis (T., 1917, **111**, 389—395).—In view of the disagreement between the results obtained by previous observers, further investigation has been made of the change in the velocity-coefficients of the inversion of sucrose and the hydrolysis of methyl acetate when the two reactions take place in the same solution. In presence of methyl acetate, the rate of inversion of sucrose is at first slightly diminished. With increasing ester concentration the velocity-coefficient passes through a minimum value, the subsequent increase being attributed to the diminution in the negative catalytic effect of water which is displaced on addition of the ester.

The presence of sucrose increases the rate of hydrolysis of methyl acetate, but when a correction is made for the influence of the displaced water, it appears that sucrose is a feeble negative catalyst. H. M. D.

Studies in Catalysis. VII. Heat of Reaction, Equilibrium Constant, and Allied Quantities from the Point of View of the Radiation Hypothesis. William Cudmore McCullagh Lewis (T., 1917, **111**, 457—469. Compare T., 1916, **109**, 796).—The idea that molecules become reactive when the energy content reaches a certain critical value is shown to be quite compatible with the fact that the reaction involved may be exothermic or endothermic. By considering the case of a unimolecular reversible reaction, it is shown that the heat of the reaction at constant volume, Q_v, is connected with the critical increments of the two kinds of molecules by the equation $+Q_v=E_2-E_1$. By introduction of the quantum hypothesis, this

assumes the form $-Q_v = Nh(\nu_1 - \nu_2)$, in which N is the Avogadro constant, h Planck's constant, and ν_1 and ν_2 the critical frequencies of the reacting and resulting molecules. This relation has been previously derived by Haber from the consideration of a somewhat special case.

From a consideration of the magnitude of the heat effects accompanying chemical reactions, it is shown that the mean internal energy of the molecules is in many cases much greater than can be accounted for by the temperature, and the conclusion is drawn that the energy content is large even at absolute zero. The temperature at which an uncatalysed reaction first proceeds with measurable velocity gives some idea of the magnitude of the energy quantum which is required to bring the molecules of a substance into the reactive condition.

The radiation hypothesis is applied to bimolecular reactions, and expressions are derived for the velocity-coefficient and the influence of temperature on the velocity. It is inferred that the higher the order of a reaction, the greater is the probable value of its temperature-coefficient.

Formation of intermediate compounds will have an influence on the magnitude of the velocity-coefficient, but the rate of change of this with temperature will not be affected if catalytic influences are excluded. H. M. D.

Evolution of the Elements and the Stability of Complex Atoms. A New Periodic System which shows a Relation between the Abundance of the Elements and the Structure of the Nuclei of Atoms. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1917, **39**, 856—879).—A theoretical paper. In previous papers (A., 1916, ii, 240) it is shown that elements are very probably interatomic compounds of hydrogen, and that one of the first steps in the formation of a complex atom is the change of hydrogen into helium. On this hypothesis, the elements are found to fall into two series: the series of even atomic number, beginning with helium and having the general formula $n\mathrm{He}'$, and the series of elements with odd atomic numbers, beginning with lithium and having the general formula $n\mathrm{He}' + \mathrm{H}'_3$. If the elements actually belong to these two series, as the hypothesis indicates, it is to be expected that the properties of the elements of the two series should indicate the differences between them. This has been shown, from the interpretation of the atomic weights in the light of the disintegration of the radioactive elements, to be the case, and consequently evidence of the validity of the present hypothesis is thus furnished. Further evidence is now put forward which is in complete accord with the system. The ordinary periodic system of the elements seems to be a relationship which expresses in a graphic way the variations in the arrangement and the number of the external electrons, especially the valency electrons, in the atom, which finds its expression in the chemical and physical properties of the elements. The hydrogen–helium system is most fundamentally related to the structure of the nuclei of the atoms,

and this structure should not affect the arrangement of the external electrons if the nucleus is extremely minute, since this arrangement would depend on the number of electrons, which in turn depends on the nuclear charge, but not on the internal structure of the nucleus except in so far as this structure affects the total charge. The structure of the nucleus should, however, affect its stability, which would have an expression in the abundance of the respective elements. There is another factor, too, which would have an effect on the abundance, and that is the relative abundance of the special materials used in the formation of the element in question.

The abundance of the elements in the earth's crust might seem to give the best information in this respect if it were not known that the surface of the earth has been subjected to very long-continued differentiative processes, and so has a very local character. The meteorites, on the other hand, come from much more varied positions in space, and at the same time show much less indication of differentiation. In the meteorites, the elements of even atomic number are on the average about seventy times more abundant than the odd-numbered elements, and, moreover, if the elements are plotted in order of their atomic numbers, it is found that the even-numbered elements are in every case very much more abundant than the adjacent odd-numbered elements. Almost more striking than this is the fact that the first seven elements in the order of their abundance are all even numbered, and, furthermore, make up 98·78% of the material. Both the iron and stone meteorites separately show just these same relations, whether the percentages are calculated as atomic or by weight. Thus the stone meteorites contain 97·6% and the iron meteorites 99·2% of even-numbered elements. It is remarkable, too, that the highest percentage found for any odd-numbered element in any class of meteorites is 1·53%, whilst among the even-numbered elements larger percentages are common, and range up to 90·6%. In the lithosphere, whilst the relationship is not so striking, the even-numbered elements are still seven to ten times as abundant as those which are odd, depending on whether the calculations are made by weight or by atomic percentage. Among the rare earths, the even-numbered elements are the more abundant. Among the radioactive elements, the odd-numbered element is in each case either of a shorter period than the even-numbered, or else is as yet undiscovered. Five elements are as yet unknown, and these are all odd-numbered. The elements of low atomic number are found to be very much more abundant than those of higher atomic number, both in the meteorites and on the earth. Thus the first twenty-nine elements make up about 99·9% of the material, whilst the remaining sixty-three are either extremely rare or comparatively rare. Of the first twenty-nine elements, those with atomic numbers between 6 and 28 include nearly all the material. The above-mentioned results seem to show that the elements fall into two series, as predicted from the helium–hydrogen structure previously described (*loc. cit.*). The variation in the abundance

of the elements as found would seem to be the result of an inorganic evolution, which is entirely independent of the Mendeléev periodic system. The formation of the elements seems to be, however, related to the atomic number. The influence of segregation on the composition of the lithosphere is discussed, as well as the effect of the stability of the atoms on their formation. The hydrogen–helium structure of the atoms would therefore seem to be a theory based on evidences as firm as a large number of the generally accepted theories of chemistry and physics, since predictions made in connexion with it have been so strikingly verified. This theory establishes to some extent a normal average composition for material, and in consequence it should have an important bearing on the history of the differentiative processes which have taken place on the earth, and its applications to geology should be far-reaching. J. F. S.

Chinese Alchemy. H. J. Holgen (*Chem. Weekblad*, 1917, **14**, 400—406).—A historical account of alchemy as practised in China, mainly with the object of discovering an "Elixir of Life." A. J. W.

[New Type of Condenser.] H. P. Fishburn (*J. Amer. Chem. Soc.*, 1917, **39**, 1074).—A piece of apparatus is described which will serve as a simple condenser when long-necked flasks are used for reflux work. The condenser consists of a thin-walled glass tube about 0·3 cm. less in diameter than the neck of the flask with which it is to be used. This tube is slightly enlarged at the top and tapered toward the bottom, so that when placed in the neck of the flask it is supported by the enlargement and leaves a space of 0·15 cm. in between the two surfaces. Into the top of the tube a narrow glass tube, which reaches to the bottom of the wider tube, is fused, and an outlet tube is sealed by the side of this at the top. When water circulates through the apparatus, a fairly efficient condenser is produced. J. F. S.

A Convenient Form of Autoclave. George W. Morey (*J. Washington Acad. Sci.*, 1917, **7**, 205—208).—The bomb of the autoclave is made from a piece of 8·7 cm. pipe, the lower end of which is closed by welding on an iron bottom. The upper end is closed by the cover, the outer rim of which presses against an inner shoulder on the outer shell, which is made from 10 cm. pipe. Closure is effected by compression of a gold wire washer, pressure being applied by a bolt threaded through a cross-bar fixed to the lower end of the outer shell.

The autoclave has given highly satisfactory results in experiments with aqueous solutions up to 300°. It is said to be superior to other forms of autoclave in ease of construction, in manipulation, and in certainty of closure. H. M. D.

Inorganic Chemistry.

Action of Sulphur Dioxide on Metal Oxides. I. DALZIEL LLEWELLYN HAMMICK (T., 1917, **111**, 379—389).—The results obtained on heating various metallic oxides in a current of sulphur dioxide show that cupric oxide, bismuth oxide, mercuric oxide, manganese dioxide, and lead peroxide may be grouped together in that the sulphur dioxide undergoes oxidation in contact with each of these. Although the sulphate of the metal is one of the products of the reaction in each case, the actual change varies with the nature of the metal.

The other oxides examined (stannous oxide, lead monoxide, ferrous oxide, and manganous oxide) behave similarly to the alkaline earth oxides in that sulphites appear to be formed as the primary product, which is subsequently transformed into a mixture of sulphides and sulphates. No indication of the actual formation of sulphites has been obtained, but, whatever the first step in the complete reaction may be, the nature of the ultimate products indicates that these oxides have a reducing effect on the sulphur dioxide. H. M. D.

Experiments with Nitrogen Trichloride. C. T. DOWELL and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 896—905).—The authors have investigated the action of a solution of nitrogen trichloride in carbon tetrachloride on a number of reducing agents. The nitrogen trichloride was prepared by the action of ammonium chloride on hypochlorous acid in the presence of carbon tetrachloride. The carbon tetrachloride solution, of about $0·1M$ concentration, was preserved in blackened bottles, in which, after some weeks, it slowly decomposed. Of all the reducing agents examined, only one, sodium sulphite, converted the whole of the nitrogen into ammonia; this occurs according to the equation $3Na_2SO_3 + NCl_3 + 3H_2O = 3Na_2SO_4 + 2HCl + NH_4Cl$. In all other cases free nitrogen was also liberated. In the case of arsenious acid ($0·123N$), 7·7% of the nitrogen is liberated, whilst on reducing the concentration by one-half, the amount of nitrogen liberated is increased fourfold. The addition of sulphuric acid increases the amount of nitrogen set free, and this amount increases up to $0·5N$-sulphuric acid, after which increased concentrations of sulphuric acid have no further action. Hydrogen sulphide sets free about 5·5% of the nitrogen in the elementary condition, the residue being reduced to ammonia. Potassium iodide liberated 18% of the nitrogen as gas. and the addition of sulphuric acid did not change this amount. The reactions with ferrous sulphate were examined, and here also nitrogen and ammonia were formed. Iodine reacts with nitrogen trichloride, setting free nitrogen and forming chlorides of iodine; on the addition of water to the resulting solution, iodic acid is precipitated.

Sodium hydroxide reacts with nitrogen trichloride, giving a rapid evolution of nitrogen, although about 7% of the nitrogen present is recovered as ammonia. Quinol is converted into hexachloroquinol, whilst carbamide in acid solution is not acted on, but in neutral solution there is a slow evolution of nitrogen. Nitrogen trichloride reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution to give nitrogen and hydrogen chloride, $NH_4Cl + NCl_3 = N_2 + 4HCl$. J. F. S.

Reactions between Chlorine and Ammonia. WILLIAM C. BRAY and C. T. DOWELL (*J. Amer. Chem. Soc.*, 1917, **39**, 905—913).—The authors tabulate the reactions which occur when ammonia and chlorine react (*a*) in acid solution, (*b*) in alkaline solution, and (*c*) in dilute solutions of ammonia and hypochlorous acid. Noyes and Lyon (A., 1901, ii, 601) have shown that when chlorine gas reacts with 0·5% ammonia solution, the reaction $3NH_3 + 6Cl_2 = N_2 + NCl_3 + 9H^+ + 9Cl^-$ takes place, in which equimolecular quantities of nitrogen and nitrogen trichloride are produced. This reaction, if it follows the equation, would be of the ninth order, and to ascertain whether this is so, a number of experiments have been carried out on the reaction between gaseous chlorine and ammonium hydroxide. From the results of these experiments, it is concluded that the above equation is only the resultant of a number of intermediate reactions, the first of which is the formation of monochloroamide, NH_2Cl, according to the equation $NH_3 + Cl_2 = HCl + NH_2Cl$. J. F. S.

Some Compounds of Boron, Oxygen, and Hydrogen. MORRIS W. TRAVERS, N. M. GUPTA, and R. C. RAY (Pamphlet, 1916, pp. 46. Compare A., 1912, ii, 938).—Further investigation of the reaction between magnesium boride and water, and of the nature of the substances present in the resulting solution, has shown that many of the conclusions drawn from the previous observations (*loc. cit.*) require correction.

The new experiments show that when a mixture of $2\frac{1}{4}$ parts of magnesium powder and 1 part of anhydrous boric acid is heated in a current of hydrogen until the reaction is complete, solutions are obtained by treatment of the product with water which are free from boric acid and magnesium borate, and contain only substances which are described as borohydrates. The main product of the action of water is an insoluble compound of magnesium oxide with a borohydrate, reaction taking place in accordance with the equation $Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2$. The soluble borohydrates and gaseous compounds of boron and hydrogen, which are also formed, are attributed to secondary reactions.

The solutions of the borohydrates are unstable, but the stability is increased in presence of traces of ammonia. On the addition of acids to the solutions, hydrogen is evolved, and the acid solutions decolorise iodine. Analyses and molecular weight determinations indicate that the mean composition of the borohydrates is

represented by $H_6B_2O_2$. When the solutions are evaporated to dryness and the residue heated, a mixture of the oxide, B_2O_2, with magnesium oxide is obtained.

If the mixture of magnesium boride and boric acid is insufficiently heated, or if excess of boric acid is employed in preparing the mixture, the solutions obtained by the action of water differ from those described above in that they contain magnesium borate and boric acid, as well as one or more borohydrates.

When magnesium boride, after prolonged treatment with water, is acted on by strong ammonia, a solution is obtained which does not lose hydrogen when kept in an exhausted tube, and does not oxidise in contact with the air. On addition of acids to this solution, hydrogen is rapidly evolved, and the acid solution reacts with iodine. When the solution is evaporated to dryness at low temperature in a vacuum, a white, crystalline residue remains which gives off hydrogen when heated, and is transformed into the oxide, B_4O_5. This oxide dissolves in water with the formation of a yellow solution, which rapidly absorbs oxygen in contact with the air, the reaction being represented by the equation $2B_4O_5 + O_2 + 12H_2O = 8B(OH)_3$.

Molecular weight determinations of the substance in the ammoniacal solution prepared as described above seem to show that the compound has the formula $H_{12}B_4O_6,2NH_3$. When ammoniacal solutions of the borohydrates are evaporated to dryness and treated with water, a small quantity of insoluble residue is left which appears to be a hydrated derivative of an oxide containing less oxygen than those previously referred to.

The constitution of the borohydrates is discussed on the basis of the chemical and physical properties of the solutions.

H. M. D.

Preparation of Carbon Suboxide from Malonic Acid and Phosphoric Oxide. ALFRED STOCK and HUGO STOLTZENBERG (*Ber.*, 1917, **50**, 498—502).—The poor yields of carbon suboxide which are usually obtained by the action of phosphoric oxide on malonic acid are largely due to the polymerisation of the suboxide under the catalytic influence of the dehydrating agent. If the suboxide is removed rapidly by carrying out the reaction in a good vacuum and condensing the product by means of liquid air, a volume of the gas corresponding with as much as 25% of the malonic acid can be obtained. An apparatus is figured and its manipulation described whereby the whole process, inclusive of the removal of the acetic acid formed, by means of a lime tower, and the fractional distillation of the carbon dioxide and suboxide mixture can be carried out in a comparatively short time.

Carbon suboxide has m. p. $-111\cdot3°$, vapour pressure at 0°, 587—589 mm., and b. p. 6°. The polymerisation of the gas to the red substance, which is soluble in water, is catalysed remarkably by the polymeride itself. The gas may sometimes be kept for days, but as soon as polymerisation sets in, it completely disappears within a day. In contact with phosphoric oxide, the gas

polymerises in a fraction of a minute. Carbon suboxide is very soluble in carbon disulphide or xylene. It is completely converted into malonic acid by means of water, so a few drops of water serve as an excellent gasometric absorbent for the gas.

J. C. W.

A Simple Method of Preparing Potassium Stannichloride. JOHN GERALD FREDERICK DRUCE (T., 1917, **111**, 418—419).—A concentrated solution containing potassium chloride and stannous chloride in the molecular ratio 2:1 is acidified with hydrochloric acid and subjected to the action of chlorine. The resulting solution yields crystals of potassium stannichloride when slowly evaporated at 50—70°. H. M. D.

New Acid Sodium Phosphate and its Action on Glass, Porcelain, Silica, Platinum, and Nickel Vessels. JOHN H. SMITH (*J. Soc. Chem. Ind.*, 1917, **36**, 419—420).—The salt is easily prepared in an impure condition by evaporating mixtures of sodium hydroxide or sodium carbonate with a sufficient proportion of phosphoric acid and igniting the residue. It forms a fused, glassy mass which dissolves slowly in cold, but more readily in warm water, and is nearly neutral to methyl-orange or phenolphthalein. The name *sodium polyphosphate* is proposed. Its powerful corrosive action renders it almost impossible to obtain the substance in a pure condition or to determine its exact composition, which, however, is probably expressed by the formula $Na_4P_6O_{17}$.

A remarkable property of sodium polyphosphate is its exceedingly energetic action on glass, porcelain, platinum, and silica vessels. The action is naturally most powerful at the high temperature of fusion, the glaze of porcelain dishes being eaten into and leaving, after solution of the salt, a deposit of granular silica. Silica vessels were also sensibly attacked, and silica entered into the composition of the resulting salt. A platinum dish was strongly attacked and became brittle wherever it had been in contact with the fused salt. A nickel vessel was corroded until the residue consisted entirely of nickel and sodium pyrophosphates. H. W.

Constitution of the Alkali Phosphates and some New Double Phosphates. JOHN H. SMITH (*J. Soc. Chem. Ind.*, 1917, **36**, 420—424).—When attempts are made to prepare disodium hydrogen phosphate by the treatment of phosphoric acid with the calculated quantity of sodium hydroxide or carbonate, the resulting solution can only be caused to crystallise with considerable difficulty. The salt which separates has the composition

$$17Na_2HPO_4,Na_3PO_4,$$

whilst the mother liquor contains the excess of phosphoric acid in the form NaH_2PO_4. The following double phosphates are also described, in which, however, the water of crystallisation, although always very considerable, has not been determined:

$$8Na_2HPO_4,Na_3PO_4,$$

thin laminæ belonging apparently to the mono- or tri-clinic systems;

$6Na_2HPO_4,Na_3PO_4$, fine, rhombic tables with angles of 66°; $3Na_2HPO_4,Na_3PO_4$, rhombic pyramids with basal planes in parallel grouping forming radiating spires; $3Na_2HPO_4,2Na_3PO_4$, fine needles.

Sodium dihydrogen phosphate crystallises as such from its aqueous solution.

Sodium polyphosphate (compare preceding abstract) could not be crystallised from water, since, on prolonged boiling, it is transformed into orthophosphoric acid and sodium metaphosphate.

Attempts are also recorded to obtain trisodium phosphate by crystallisation from solutions of equivalent quantities of phosphoric acid and sodium hydroxide; the crop so obtained had the approximate composition $2Na_3PO_4,Na_2HPO_4$, whilst the mother liquor gave feathery crystals of the composition $18Na_3PO_4,Na_2O$. A similarly constituted salt was obtained by direct crystallisation when a 4% excess of sodium hydroxide was used.

In the manufacture of trisodium phosphate, the best method appears to consist in the use of sodium carbonate for the first stage and sodium hydroxide for the second stage, employing the proportions indicated by the equations: $36H_3PO_4 + 37Na_2CO_3 = 34Na_2HPO_4 + 2Na_3PO_4 + 37CO_2 + 37H_2O$ and

$$34Na_2HPO_4 + 2Na_3PO_4 + 38NaOH = 36Na_3PO_4 + 2Na_2O + 36H_2O$$

H. W.

Ammonium Thiosulphate - Polythionate Solutions. A Contribution to Liquid Purification of Coal Gas. E. V. Espenhahn (*J. Soc. Chem. Ind.*, 1917, **36**, 483—489).—The actions occurring between ammonium thiosulphate, ammonium polythionate, sulphur dioxide, and ammonia have assumed practical importance since the introduction of the Feld method of utilising the sulphur contained in the coal for the fixation of ammonia without first forming sulphuric acid (compare A., 1912, ii, 448). The following are the chief results of an investigation of the interaction of these substances.

The reaction between thiosulphate and sulphur dioxide is expressed by the equation: $2(NH_4)_2S_2O_3 + 3SO_2 = (NH_4)_2S_3O_6 + (NH_4)_2S_4O_6$. Under certain conditions, other reactions occur according to the equations (1) $2(NH_4)_2S_2O_3 + 3SO_2 + S = 2(NH_4)_2S_4O_6$, and (2) $2(NH_4)_2S_4O_6 = (NH_4)_2S_3O_6 + (NH_4)_2S_5O_6$; these, however, do not influence the main reaction.

Although the reaction between polythionate and ammonia solution as expressed by the products of the reaction appears uniform, it actually proceeds between two extremes represented by the equations: $3(NH_4)_2O,OH_2 + 2(NH_4)_2S_nO_6 = 5(NH_4)_2S_2O_3 + 3H_2O$ (where $n = 5$), and $(NH_4)_2O,OH_2 + (NH_4)_2S_nO_6 = (NH_4)_2S_2O_3 + (NH_4)_2SO_4 + H_2O$ (where $n = 3$).

The reactions between tri-, tetra-, and penta-thionate and potassium or sodium hydroxide may take place separately according to equations: $10KOH + 2(NH_4)_2S_5O_6 = 5K_2S_2O_3 + 4NH_3 + 7H_2O$; $6KOH + 2K_2S_4O_6 = 3K_2S_2O_3 + 2K_2SO_3 + 3H_2O$; and

$$6NaOH + 2Na_2S_3O_6 = Na_2S_2O_3 + 4Na_2SO_3 + 3H_2O.$$

The velocities of the five above-mentioned reactions greatly increase with rise of temperature.

Sulphur dioxide is not absorbed by ammonium thiosulphate in the presence of ammonia unless polythionate is present in the solution. It is then added to form polythionate, which does not decompose to sulphate at 100°, so that the amount of sulphate formed for each ammonium concentration is the same as with polythionate and ammonia.

When ammonia acts on ammonium polythionate and sulphur dioxide in the presence of hydrogen sulphide (that is, ammonia and ammonium sulphide), less sulphate is formed than in the absence of hydrogen sulphide and the velocity of the reaction is considerably greater.

Certain modifications of the Feld process for ammonia recovery are suggested. H. W.

Solubility of Calcium Sulphite in Water and Sugar Solutions. T. VAN DER LINDEN (*Mededeel. Proefstat. Java Suckerindustrie*, 1916, **6**, 307—322; from *Chem. Zentr.*, 1917, i, 366).—The experiments were performed by titrating 100—200 grams of solution with $N/100$-iodine. The results show that the solubility of calcium sulphite in water and sugar solutions is very slight. In the latter case the solubility is greater than in the former and is greatly depressed by the presence of gypsum. The solubility of calcium sulphite diminishes with rising temperature.

H. W.

Effect of Adsorption on the Physical Character of Precipitated Barium Sulphate. HARRY B. WEISER (*J. Physical Chem.*, 1917, **21**, 314—333).—The conditions which affect the form in which barium sulphate is precipitated are discussed by the author, and a series of experiments is described which indicates the effect, on the nature of the precipitate, when barium sulphate is formed under different conditions. It is shown that barium sulphate has a marked tendency to adsorb many other substances. Since any substance which is adsorbed by a second will tend to peptise the latter, it follows that, other conditions being the same, barium sulphate will be deposited in the most finely divided state when precipitated in the presence of those substances for which it has the greatest specific adsorption. In accordance with the general rule, barium sulphate shows a marked adsorption for its own ions. Positive colloidal solutions of barium sulphate, stabilised by preferential adsorption of barium ion, have been prepared by Kato and Recoura (A., 1910, ii, 850; 1908, ii, 692); the present author has now prepared a negative colloidal solution of barium sulphate, stabilised by preferential adsorption of sulphate ions. This was done by adding $0 \cdot 1N$-sodium sulphate in slight excess to a $0 \cdot 1N$-solution of barium chloride in a 1 : 5 glycerol–water solution. Barium sulphate is deposited in a much finer state when precipitated with barium chloride in excess than with sulphuric acid in excess. Finer crystals are also obtained from potassium sulphate solutions. This is ex-

plained as follows. Barium sulphate adsorbs its own ions strongly and hydrogen ions are much more strongly adsorbed than other cations. When sulphuric acid is precipitated by barium chloride, the precipitate tends to deposit in a finely divided state because of the relatively strong adsorption of barium ions and hydrogen ions. It would also be deposited very finely divided from sulphuric acid solution were it not that the strongly adsorbed hydrogen ion diminishes the adsorption of the sulphate ion. From potassium sulphate solution it is precipitated finely divided, since the potassium ion is not strongly adsorbed. In the presence of hydrochloric acid, barium sulphate is deposited more finely divided with the barium ion in excess than with the sulphate ion in excess. In the first case, the cations hydrogen and barium are strongly adsorbed; in the second case, the presence of the sulphate ion diminishes the adsorption of the hydrogen ion. Barium sulphate is always more coarsely crystalline when precipitated in the presence of an appreciable amount of hydrochloric acid. This is due to the solvent action of hydrochloric acid. In the presence of considerable excess of hydrochloric acid the solvent action of the hydrochloric acid is the predominant factor. J. F. S.

Physico-chemical Foundations of the Commercial Zinc Extraction. M. BODENSTEIN and SCHUBART (*Zeitsch. Elektrochem*, 1917, **23**, 105—116).—The temperature at which the system zinc oxide and carbon under four different pressures (28 mm., 87 mm., 266 mm., and 760 mm.) is converted into zinc vapour and carbon monoxide has been measured. Three different methods were employed: (1) thermal analysis, (2) observation of the point at which the mixed materials lost weight, and (3) measurement of the velocity of the evolved gases. In all cases approximately the same temperature was obtained, 1033°, which is the same as that previously obtained by Johnson (*Electrochemical Industry*, 1904, 185). These values were regarded as equilibrium values and used to calculate the heat of the reaction, whereby impossible values were obtained. Consequently, the observed temperatures represent points at which the reaction is sufficiently rapid to be observed. The true equilibrium was obtained in a quartz apparatus; this set in extremely slowly, but a pressure of 1 atmosphere was obtained at 780°. An exact calculation of the experimental results has not been possible, since for this a knowledge of the vapour pressure of zinc and of the equilibrium between carbon, carbon monoxide, and carbon dioxide is necessary, and these are not known with sufficient accuracy. The possibility of extracting zinc by the use of high pressures or catalysts in a reducing atmosphere is discussed.

J. F. S.

Zinc Chromates and their Significance for the Colour Industry. LAURENZ BOCK (*Kolloid Zeitsch.*, 1917, **20**, 145—150). —A discussion of the various basic zinc chromates and alkali zinc chromates which have been described in the literature with reference to the use of zinc yellow in the pigment industry. H. M. D.

Zinc Platinichloride. AUGUST EBERHARD (*Arch. Pharm.*, 1917, **255**, 65—72).—In endeavouring to prepare a platinichloride of the reduction product obtained by the action of zinc and dilute sulphuric acid on bromoscopoline, the author obtained red crystals of the composition $ZnPtCl_6,6H_2O$, whereas, according to the earlier descriptions of zinc platinichloride, this salt is yellow. Careful examination showed that the red colour was due to the presence of a little zinc platinibromide as impurity.

In dry air the platinichloride hexahydrate is stable, but in moist air it slowly deliquesces. Contrary to the statement of Topsoë (*Oversigt K. Danske Videnskab. Selsk*, 1868, 151), the hexahydrate does not lose $4H_2O$ at 100—100·5°, but a temperature of 102—103° is necessary; the remaining $2H_2O$ is slowly eliminated above 130°.

D. F. T.

General Method for obtaining Metals in a Metalloidal Condition. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1295—1314).—The author gives the results of the application of the views previously expressed to various regions of physicochemical phenomena (A., 1913, ii, 753; 1915, ii, 411; 1916, ii, 185).

Investigation of the colour of disperse systems with metallic disperse phases and of the colour of the disperse molecules with the aid of the ultramicroscope shows that, as regards their colour, such systems form two groups. The first contains relatively coarsely-disperse systems, and the disperse particles in them still retain metallic reflection and dispersion, and the second the comparatively highly disperse systems with disperse particles exhibiting the optical properties of non-metallic substances, that is, of substances with so-called internal colour. In the first group the colour changes with the degree of disperseness exactly as in coarsely disperse systems of metalloidal selenium, and in the second group as with a transparent, coloured substance which absorbs the red and blue parts of the spectrum and transmits orange, yellow, and green light.

These two groups of disperse systems of one and the same element contain the latter in two different states, namely, the metallic and the metalloid, the optical properties being different in the two cases. No sharp line separates these two states, intermediate stages being quite possible. Such measurements as those of Galli ("Das optische Verhalten dünner Metallschichten," Diss., Göttingen, 1913) on the index of refraction of thin layers of silver deposited on glass by cathodic disintegration show that at a sufficiently high degree of dispersion even typical metals pass from the metallic to the metalloidal condition. The value of the refractive index of the transparent, intensely coloured metalloidal substance then obeys the same rule as for all metalloids.

Of the three known modifications of selenium, the author has investigated two: (1) the red, crystalline metalloidal form which melts at 170—180° when rapidly heated and at 150° is converted into the metallic modification melting at 217°. The latter form is

not transformed on cooling into the red variety, which is obtainable only by quickly cooling the fused metallic selenium from a temperature of 250°. Thus, in the coarsely disperse condition, on rise of temperature, red metalloidal selenium ⟶ grey metallic selenium. If, however, the condition is sufficiently highly disperse, the reverse change may be induced. Further, Saunders found that grey metallic selenium, when finely powdered, is converted into the red metalloidal form, which at about 200° is transformed into the grey variety, and so on

The conditions which give rise to the metallic and metalloidal states are discussed and also the regions over which they are capable of existing. T. H. P.

Arsenates of Lead. III. Basic Arsenates. C. C. McDONNELL and C. M. SMITH (*J. Amer. Chem. Soc.*, 1917, **39**, 937—943. Compare A., 1916, ii, 620; this vol., ii, 33).—The basic lead arsenate, $8PbO,As_2O_5,\frac{1}{2}H_2O$, was first prepared by Strömholm (A., 1904, ii, 258); the authors have confirmed the formation of this compound, and have shown that it may be obtained by dissolving dilead arsenate in a 10% solution of sodium hydroxide to saturation, filtering, and pouring the solution into about five times its volume of boiling water. On cooling, very thin, square plates separate, which are biaxial and positive. They have D_{15}^{15} 8·04, and may be fused without change except for the loss of water. The authors term this substance octa-lead arsenate. The basic lead arsenate, $Pb_4(Pb\cdot OH)(AsO_4)_3,H_2O$, prepared by the action of ammonia on dilead arsenate, has been obtained crystallised in hexagonal prisms terminated by the basal pinacoid, frequently with the corners truncated by the second order pyramid. They have parallel extinction and are uniaxial with low negative birefringence; the average index of refraction is about 2·09. D 6·86. These crystals are similar to the crystals of mimetite; consequently, the authors have termed this substance *hydroxymimetite*. A new basic lead arsenate, $Pb_5[Pb(OH)]_2(AsO_4)_4$, is obtained by saturating 10% potassium hydroxide with dilead arsenate and pouring the solution into twenty times its volume of boiling water. On cooling, small, prismatic crystals separate which have D_{15}^{15} 7·08; they are doubly refractive, with parallel extinction, negative elongation, and index of refraction 2·07. J. F. S.

Polysilicates and Polyplumbates. GEORG KASSNER (*Arch. Pharm.*, 1917, **255**, 130—134).—In a commentary on Pukall's paper on the hydrothermal decomposition of polysilicates (A., 1916, ii, 322), the author directs attention to his work on polyplumbates (A., 1895, ii, 14; 1896, ii, 247), in which calcium di- and tetraplumbates were described. The more recent discovery of lead triplumbate, $Pb<^{O}_{O}>Pb<^{O}_{O}>Pb<^{O}_{O}>Pb<^{O}_{O}>Pb$, by Fischer and Ploetze (A., 1912, ii, 555) serves to bring lead still further into line with silicon in the production of poly-acids. In the case

of tin, the compound $H_2Sn_5O_{11}$ is the only representative known as yet.

There is one outstanding difference between polyplumbates and polysilicates, however. Whereas the former are produced by the hydrothermal treatment of ortho-plumbates, the latter suffer decomposition when heated with small quantities of water under pressure. J. C. W.

Influence of Arsenic in Brass. OLIVER SMALLEY (*J. Soc. Chem. Ind.*, 1917, **36**, 429—439).—The author has carried out an extensive investigation on the influence of arsenic in brass, and draws the following conclusions. Arsenic renders brittle all copper–zinc alloys, commercially known as 'brass,' when it is present as free arsenide; this compound is a weak, brittle constituent, and, if present in sufficient quantity, completely envelops each crystal grain, thus producing a crystalline mass the grains of which are stronger than the junctions. It therefore acts in the same manner as antimony, bismuth, and other metals which form definite intermetallic compounds the presence of which produces 'intercrystallinity.'

The films of arsenide do not affect the cold-working properties of α-brasses to any appreciable extent owing to the ready accommodation of this class of brasses to plastic deformation without rupture.

Small quantities of arsenic (under 0·10%) are beneficial to α-brasses, no matter what their physical condition; this is due to the arsenic entering mainly into solid solution, the amount remaining as free arsenide being negligible when considered as a mechanical enclosure.

A complete recovery of the ductility of all essentially cold-working arsenical brasses containing under 0·5% arsenic is effected by cold-working and subsequent annealing, this treatment causing a complete solution of arsenide which is beneficial to the quality of the brass when present in quantities not exceeding 0·20%; between 0·2% and 0·5% the brass possesses the same properties as a non-arsenical brass. When the arsenic present exceeds 0·5%, the brass becomes intercrystalline whatever the physical condition of the arsenide may be. It thus appears that the physical properties of arsenical α-brasses containing less than 0·5% As are governed by the physical condition of the brass; when exceeding that amount, the percentage of arsenic governs the physical properties, no matter what be the physical condition of the alloy.

The temperature at which α-phase brasses containing free arsenide will anneal is 30—50° higher than that of pure non-arsenical brass; data are not yet available concerning the influence of arsenic on recrystallisation when present in perfect solid solution in the copper–zinc as a perfectly homogeneous alloy.

Arsenic when present even in the most minute quantities is detrimental to the physical properties of hot-worked brass, although it in no way affects the hot-working properties.

Arsenic does not assist in any structural inversion of the β-constituent when cooled under normal conditions. H. W.

Composition of a Bronze Age Wind Instrument. F. RATHGEN (*Zeitsch. anal. Chem.*, 1917, **56**, 144—148).—The tubular portion of the instrument examined consisted of: copper, 85·03%; tin, 13·76%; lead, 0·10%; iron, 0·37%; cobalt, 0·54%; arsenic and sulphur, traces. Other portions of the instrument had similar, but slightly different, compositions. W. P. S.

An Improved Mercury Still. L. H. DUSCHAK and S. O. SPENCER (*J. Physical Chem.*, 1917, **21**, 311—313).—A modification of the Weinhold mercury distillation apparatus is described; it consists of the ordinary vacuum distillation apparatus, to which a device is added whereby a small quantity of air is allowed to bubble into the distillation bulb at a definite rate. By this means the distillation takes place in a partial vacuum and not in a Torricellian vacuum as hitherto. The advantage claimed for the modified apparatus is that those metals which generally accompany mercury are oxidised during the distillation and are thereby more effectively separated than by ordinary distillation. J. F. S.

Some Rare Earth Compounds. A. J. GRANT and C. JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 933—937).—With the object of finding methods for rapidly separating the rare earth compounds, the authors have determined the solubility of a number of oxalates in 20% solutions of methylamine oxalate, ethylamine oxalate, and triethylamine oxalate. The following amounts of rare earth oxalate, expressed in grams of M_2O_3, dissolve in 100 c.c. of the solution: (i) Methylamine oxalate, neodymium, 0·027; gadolinium, 0·069; dysprosium, 0·276; yttrium, 0·877; thulium, 4·082; and ytterbium, 5·242. (ii) Ethylamine oxalate, neodymium, 0·107; gadolinium, 0·360; dysprosium, 1·787; yttrium, 1·653; thulium, 5·728; and ytterbium, 5·858. (iii) Triethylamine oxalate, lanthanum, 0·032; neodymium, 0·065; gadolinium, 0·883; dysprosium, 1·432; yttrium, 1·006; thulium, 1·340; and ytterbium, 2·048. These figures indicate that there is no great variation in the series of the solubilities. Several new salts are described. *Neodymium diphenylsulphonate*, $(C_6H_5\cdot C_6H_4\cdot SO_2\cdot O)_3Nd,6H_2O$, is prepared by adding an acidified solution of the sodium salt to a solution of neodymium chloride; the salt is sparingly soluble in water and separates as a mass of light pink crystals. *Neodymium ferricyanide*, $NdFe(CN)_6,4H_2O$, is formed when a mixture of concentrated solutions of potassium ferricyanide and neodymium chloride is boiled. The salt separates as a brick-red powder which has an orange tint and is very slightly soluble in water. *Lanthanum ferricyanide*, $LaFe(CN)_6,4H_2O$, is prepared in the same way as the neodymium salt; it is slightly more soluble and does not possess such a rich colour. *Yttrium ferricyanide*, $YFe(CN)_6$, is precipitated from a mixture of dilute solutions of potassium ferricyanide and yttrium chloride. The ferricyanides of erbium, thulium, and ytterbium are less soluble than the yttrium salt; hence the precipitation of the ferricyanide would appear to be a possible method for the separation of the yttrium earths. This was proved in the

following case: an impure yttrium preparation containing erbium and of mean atomic weight 104·90 was dissolved in hydrochloric acid, the solution just neutralised, and boiled. To the boiling solution potassium ferricyanide was added. The precipitate was treated with sodium hydroxide, filtered, washed, dissolved in hydrochloric acid, and precipitated with oxalic acid. The oxalate was ignited, and the process repeated with the filtrate and a second fraction obtained. The fifth fraction had a mean atomic weight of 93·00. The authors emphasise the fact that the yttrium earth ferricyanides are considerably less soluble than has hitherto been believed, and express the opinion that the above method of separation is the most rapid known.

In connexion with the preparation of neodymium diphenylsulphonate, the authors experienced difficulty in the preparation of diphenyl by the method of passing benzene vapour through a hot tube, and have devised a method of preparing this substance which rapidly gives a good yield of the hydrocarbon. A quantity of benzene is placed in a wide-necked flask, fitted with a condenser, in which above the benzene layer a length of nichrome ribbon is suspended. The ribbon is connected with an alternating circuit. The benzene is boiled for a few minutes by means of a flame, and then current is allowed to flow through the ribbon so that it is raised to dull redness. The flame is then extinguished and the benzene kept boiling for five to seven hours by the heat from the wire. At the end of this period the liquid in the flask will solidify when cooled. J. F. S.

The Action of Acetic Acid on Aluminium. RICHARD SELIGMAN and P. WILLIAMS (*J. Soc. Chem. Ind.*, 1917, **36**, 409—415. Compare A., 1916, ii, 187).—In continuation of their previous experiments, the authors have investigated the action of boiling dilute acetic acid, and also of acetic acid of all concentrations at the ordinary temperature, on aluminium. In addition, the effect of the presence of small quantities of various substances in the acetic acid has been determined.

The aluminium, containing Al=99·1%, Si=0·45%, Fe=0·45%, Cu=0·00%, was used in the form of thin, rolled strips which were generally annealed at 450° for three hours before use. The surface was cleaned with sodium hydroxide and washed with dilute nitric acid previous to determining the rate of dissolution.

As in the case of the more concentrated acids, the rate of dissolution of aluminium in boiling dilute acetic acid is found to rise continuously until the concentration of the acid falls to 1%. With more dilute acid, it is impossible to obtain trustworthy data as the metal becomes coated with a protective skin. The rate of dissolution is greatly affected by the products of the interaction, the disturbance growing very rapidly with increasing dilution. A definite reason cannot yet be assigned, but it has been shown that acid which has become highly active towards aluminium can be distilled without change in its activity.

Solutions of acetic acid boiled in contact with aluminium become

turbid after a period which is short or long according to the concentration of the acid; the nature of the turbid solutions varies in the different cases. With acids of concentration between 60% and 5% the turbidity disappears on keeping or on addition of dilute hydrochloric acid. Little or no deposit is formed on the aluminium strip, and if any deposit is formed it is always loosely attached and readily removable. Such turbidity appears to be due to the separation of basic acetate or acetates of aluminium. In the case of acids of about 0·2% concentration, the turbid solutions do not become clear on keeping, and the addition of dilute hydrochloric acid or sodium hydroxide produces a flocculent precipitate which does not readily dissolve in boiling dilute hydrochloric acid. Such solutions give rise to a deposit which adheres firmly to the aluminium and is not readily removed either by chemical or mechanical means. It is considered that in these cases the turbidity may be due to the formation of a colloidal solution of aluminium hydroxide. Solutions containing between 5% and 0·2% of acetic acid yield turbid solutions of an intermediate character.

Except in the case of the anhydrous acid, aluminium is uniformly attacked by boiling acetic acid at all concentrations; no evidence of local action has been observed.

In general, aluminium is only slowly attacked by cold acetic acid; the rate of dissolution increases with increasing dilution of the acid, the highest rate so far observed occurring with an acid containing 0·02% acetic acid. The rate is frequently high at first, but rapidly falls, and then remains constant over long periods. In most cases the attack is uniform, but local action has been observed at concentrations between 70% and 95%, and in cases in which the metal has been allowed to remain in contact with thin films of dilute acid which have thereby become subjected to extensive aeration. The main factor in determining local action appears to be the presence of oxygen, although there is evidence that some other factor also plays a part.

The action of boiling acetic acid (about 10%) on aluminium is practically unaffected by the addition of up to 1% of sodium chloride, potassium bromide, iodide, or nitrate, whereas an equivalent amount of sodium sulphate raises the rate of dissolution appreciably. With the cold acid, on the other hand, the rate of dissolution is increased tenfold by 1% of sodium chloride, whereas potassium bromide effects a smaller increase and potassium iodide and nitrate are without action; 0·5% of sodium sulphate causes a fourfold increase in the rate of dissolution. With cold concentrated acid (about 80%) a marked increase is produced by 1% of sodium chloride, a smaller increase by potassium bromide or iodide, no effect by sodium sulphate, and a decrease by potassium nitrate. The most serious effect of the addition of substances was noted in the case of the boiling, 80% acid. Here the rate of dissolution is raised by 1% of sodium chloride from 290 to 16,000; by 1% of potassium bromide the rate is only increased from 290 to

485, whilst potassium iodide and potassium nitrate are practically without effect. Sulphuric acid (0·5%) in the form of sodium sulphate somewhat increases the rate of dissolution.

The enhanced effect of chlorides as compared with bromides is shown to be due to the fact that aluminium is more readily attacked by hydrochloric than by hydrobromic acid. The influence of iodides in cold solution is due to the separation of free iodine; if the latter is removed the rate of attack falls to that of the acid alone.

In cases in which the acid alone attacks aluminium uniformly, a uniform attack was also observed in the presence of the salts investigated; where, however, the acids alone caused local action, such action was generally promoted by the presence of halogens, retarded by small quantities of sulphuric acid, and absolutely inhibited by as little as 0·1% of nitric acid. H. W.

The Refractory Properties of Clay. H. LE CHATELIER and F. BOGITCH (*Compt. rend.*, 1917, **164**, 761—767. Compare Mellor and Moore, *Trans. English Ceramic Soc.*, 1916, **15**, 77).—An examination of the behaviour of clays of varying composition when submitted to varying pressures at high temperatures. Up to 1100° the resistance to pressure remains invariable. At higher temperatures the material yields increasingly and becomes plastic, the resistance falling rapidly above 1200°. The effect of varying the three factors, time, pressure, and temperature, has been studied. With pressures of 10 kilos. and 1 kilo./cm.^{2} the differences between the temperatures causing the same yielding of the clay are much less than might be expected, not reaching 50° for this pressure range. Varying the temperature of preliminary heating of the brick from 1200° to 1430° has much the same effect. Increasing the purity of the clay used increases the resistance of the brick to temperature and pressure. W. G.

Constitution of Manganic Compounds. M. SEM (*Zeitsch. Elektrochem.*, 1917, **23**, 98).—Polemical, in which the author defends his position (A., 1915, ii, 777) against the criticism of J. Meyer (A., 1916, ii, 483). J. F. S.

The Nature of Subsidiary Valencies. XIV. Influence of Valency on the Energy of Subsidiary Valencies. FRITZ EPHRAIM and SEB. MILLMANN (*Ber.*, 1917, **50**, 529—541).—It was to be expected from the Abegg-Bodländer theory that the stability of metal ammines would rise with increasing valency of the central metallic atom, and so, in order to demonstrate this, the vapour tensions of ferrous and ferric, chromous and chromic, thallous and thallic, and platinous and platinic hexammines have been measured. The equilibria are particularly difficult to reach in the case of tervalent metals, owing to the formation of solid solutions on decomposition, but the data are in agreement with the expectation, except in the case of iron, in which the ferrous hexammines are the more stable.

Ferric Compounds. [For the ferrous compounds see A., 1913, ii, 496.]—The following *ammines* are mentioned: $Fe_2(SO_4)_3,12NH_3$; $FeBr_3,6NH_3$, a dark brown, granular powder; $FeCl_3,6NH_3$, a very voluminous, pale yellow powder, which is unique in being more stable than the corresponding bromide.

In order to test whether the ferric chloride hexammine just mentioned really has the unusual stability, an attempt was made to prepare it from the double salt, K_2FeCl_5. This absorbs ammonia much more slowly than ferric chloride, and the *hexammine* decomposes at a much lower temperature. It appears, therefore, that the double salt as such forms a hexammine, and not that it is first dissociated to give the ammine of ferric chloride. It is not common to get ammines of double salts, for in most cases dissociation takes place. Thus, the red salt, $KCuCl_3$, gives merely the hexammine of cupric chloride, and double alkali–nickel chlorides give the hexammine of nickel chloride. (These double chlorides are obtained by melting the component chlorides together. The fusion is indigo-blue, but passes through reddish-brown to yellow.)

Aluminium Compounds.—The aluminium haloids absorb at least six molecules of ammonia at the ordinary temperature, and the stability of the ammines varies from one halogen to the other many times more than in any other observed case.

Chromium Compounds.—White chromous chloride forms a violet triammine and an ashy-grey hexammine. The following chromic salts are mentioned: $Cr(NO_3)_3.6NH_3$ explodes on heating quickly; $[Cr(NH_3)_6](NO_3)Br_2$, long, yellow prisms; $Cr_2(SO_4)_3,6NH_3$; the hexammines (?) of the haloids and phosphate give no trustworthy tension data.

Thallium Compounds.—Thallous sulphate and chloride do not react with ammonia; the thallic salts give the *ammines*, $Tl_2(SO_4)_3,10NH_3$, and $[Tl(NH_3)_6]TlCl_6$.

Platinum Compounds.—Platinous chloride gives a tetrammine and a pentammine, and the iodide combines with 2, 4, and 6 molecules of ammonia. J. C. W.

History and Preparation of Cobalt Hygrometers. LUDWIG VANINO (*Arch. Pharm.*, 1917, **255**, 81—85).—Although cobalt salts were used in sympathetic inks as long ago as 1706 (see A., 1916, ii, 135) it was not until about 1870 that they began to be used in toy hygrometers. J. C. W.

Recovery of Molybdic Acid. PAUL RUDNICK and R. D. COOKE (*J. Ind. Eng. Chem.*, 1917, **9**, 109—110).—Molybdic acid may be recovered from titration liquors and filtrates containing excess of ammonium molybdate by adding an excess of ammonium phosphate, the collected yellow precipitates being washed by decantation with hot water and dried on a steam-bath. Five hundred and ten grams of the dried salt, containing about 92% of molybdic acid, are dissolved in ammonium hydroxide, and 85 grams of magnesium nitrate are added. After keeping two to three hours, the

clear, supernatant liquid is tested for phosphorus by adding a small quantity to twice its volume of nitric acid, when, in the absence of a yellow precipitate, the magnesium ammonium phosphate is filtered off, the filtrate made up to 2000 c.c., and added slowly, with constant stirring, to 2000 c.c. of concentrated nitric acid diluted to 4668 c.c. with water. After keeping for several days and filtering, a further 320 c.c. of concentrated nitric acid are added and the solution is ready for use. G. F. M.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphoric Acid. H. KINDER (*Stahl u. Eisen*, 1916, **36**, 1094; from *Chem. Zentr.*, 1917, i, 530).—The following method is stated to be more simple than that described by Friedrich (A., 1916, ii, 490). The molybdic acid is precipitated by adding sodium phosphate to the solution, and the yellow precipitate is washed, by decantation, with 0·1% sodium sulphate solution until free from soluble phosphate and iron salts. The precipitate is then dried; each 325 grams of it is dissolved in 1100 c.c. of ammonia ($D=0·96$), the solution is treated with a mixture of 30 grams of magnesium chloride and 30 grams of ammonium chloride dissolved in water to make 100 c.c.; the precipitate is separated by filtration, and each 420 c.c. of filtrate is mixed with 1200 c.c. of nitric acid (D 1·2). The blue molybdic acid residues obtained in the gravimetric estimation of phosphoric acid may be treated in a similar way (dissolved in ammonia, acidified with nitric acid, precipitated with sodium phosphate, etc.).

W. P. S.

Preparation of Pure Zirconium Oxide Free from Iron. K. LEUCHS (D.R.-P., 295246; addition to D.R.-P., 285344; from *J. Soc. Chem. Ind.*, 1917, **36**, 503).—A solution of crude zirconium oxide in hydrochloric acid is treated with sulphuric acid ($3ZrO_2:2H_2SO_4$) and left in the cold or at 40°. Zirconium sulphate separates in small prisms which are free from iron and also titanium. H. W.

The Zirconyl Bromides. ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 816—818).—By the evaporation of a solution of zirconium hydroxide in hydrobromic acid on a water-bath, the hydrate of zirconyl bromide, $ZrOBr_2,8H_2O$ (compare Weibull, A., 1887, 778), was obtained. The author was unable to confirm the existence of the hydrates described by Knopp (compare *Annalen*, 1871, **159**, 36) and Paijkull (compare this Journal, 1873, 1105). The octahydrate when dried in a current of dry air or in a vacuum gives the hydrate $ZrOBr_2,3·5H_2O$, which is stable up to 60—70°. Above this temperature it loses water and hydrogen bromide, giving the compound $ZrOBr_2,ZrO_2$. This basic bromide is also slowly deposited from an $N/100$-solution of zirconyl bromide on long keeping. By the addition of ether to an alcoholic solution of zirconyl bromide, the *compound*, $ZrOBr_2,ZrO_2,12H_2O$, is obtained. In a current of hydrogen bromide at a red heat the basic bromide is converted into zirconium bromide, $ZrBr_4$. W. G.

Zirconium Fluorides and Zirconyl Fluorides. ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 727—729).—The author considers that the substance, described in the literature as a hydrate of zirconium fluoride, $ZrF_4,3H_2O$, is really a hydrate of acid zirconyl fluoride, $ZrOF_2,2HF,2H_2O$. At 140° in dry air it loses two molecules of water, giving the anhydrous acid fluoride, which, when heated above 140° in air, loses two molecules of hydrogen fluoride, giving zirconyl fluoride, $ZrOF_2$; this, when cold, re-absorbs two molecules of hydrogen fluoride. The anhydrous normal zirconyl fluoride may also be obtained by crystallising the hydrated acid fluoride from dilute aqueous solution and drying the product, $ZrOF_2,2H_2O$, at 120°. If the anhydrous or hydrated acid fluoride is heated at 200° in an atmosphere of hydrogen fluoride, zirconium fluoride, ZrF_4, is obtained, which, in the cold, absorbs hydrogen fluoride, probably to form fluozirconic acid, H_2ZrF_6. W. G.

The Properties and Constitution of some New Basic Salts of Zirconium. ERNEST HARRY RODD (T., 1917, **111**, 396—407).—From a basic zirconium sulphate of indefinite composition, precipitated by partly neutralising with ammonia an acid solution of zirconium sulphate, a new basic zirconium chloride, $Zr_5O_8Cl_4,22H_2O$, has been prepared. It is a crystalline salt, readily soluble in water, less so in hydrochloric acid solution, from which it can be recrystallised unchanged. The new 5:4 basic zirconium chloride is sharply distinguished from the common oxychloride, $ZrOCl_2,8H_2O$, by its property of forming with a solution of any sulphate an insoluble basic zirconium sulphate of corresponding composition, $Zr_5O_8(SO_4)_2,xH_2O$, x being about 14. From either the new basic chloride or sulphate can be prepared a new hydroxide, distinct from normal zirconium hydroxide in that, when dissolved in hydrochloric acid, it forms a solution of the new 5:4 basic chloride. By analogy, its composition is given as $Zr_5O_8(OH)_4$. It is suggested that the new salts have structural formulæ of the type $Zr(O{\cdot}ZrO{\cdot}Cl)_4$, which would account for the remarkable stability of the salts.

The changes undergone by a solution of zirconyl chloride when boiled are discussed (compare Ruer, A., 1905, ii, 41, 827), and also the formation of metazirconic acid. It is argued that the same property which leads to the formation of the many basic salts of zirconium eventually leads to the production of metazirconic acid. The hydrolysis of the salts in solution is followed by condensation of the hydrolysed molecules, with production of complex basic salts; when this process is pushed to the limit, metazirconic acid is formed. E. H. R.

The Compounds of Zirconium Oxide with Sulphuric Acid. ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 864—865).—Mixtures of varying molecular proportions of zirconium oxide and sulphuric acid were made and dried at 200°, the densities of the resulting products being determined. The results obtained indicate the

existence of the six sulphates: $Zr(SO_4)_2$, $Zr(SO_4)_2,ZrO_2$, $5Zr(SO_4)_2,7ZrO_2$, $3Zr(SO_4)_2,5ZrO_2$, $Zr(SO_4)_2,2ZrO_2$, $Zr(SO_4)_2,3ZrO_2$.
W. G.

Enantiotropy of Bismuth. J. WÜRSCHMIDT (*Jahrb. Min.*, 1917, i, *Ref.* 2; from *Festschrift Elster-Geitel*, 1915, 326—332).—The specific gravity of bismuth determined for a mass and for the powder is 9·80 and 9·70 respectively. This suggests that during the powdering the material passes over into a lighter modification, Bi_{β}, which is perhaps identical with that described by Cohen and Moesveld (A., 1914, ii, 779), and also recognised by the author in bismuth amalgam (A., 1916, ii, 517). L. J. S.

Osmium Dioxide. OTTO RUFF and HANS RATHSBURG (*Ber.*, 1917, **50**, 484—498).—The preparation and properties of various samples of osmium dioxide are described. The work was undertaken with the view of determining the atomic weight of osmium by reducing the oxide to the metal, but this has been abandoned owing to the difficulties.

Colloidal Solutions of Osmium Dioxide.—These solutions can be obtained by the reduction of alkali osmates with alcohol or by the hydrolysis of osmichlorides, thus: $K_2OsO_4 + 2H_2O + EtOH = OsO_2,2H_2O + 2KOH + C_2H_4O$; $K_2OsCl_6 + 4H_2O = OsO_2,2H_2O + 2KCl + 4HCl$. By the addition of sufficient quantities of electrolytes to the neutral solutions, the dioxide can be precipitated, but it forms a colloidal solution again when treated with acids, alkali hydroxides, or ammonia or washed free from electrolytes. Concentrated solutions appear black by reflected light or blue by transmitted light.

Pyrophoric Osmium Dioxide.—The oxide prepared by reduction or by the hydrolysis of ammonium osmichloride retains alkalis and organic substances very firmly. As a result, the dry powder is more or less dangerous to handle, as it may kindle on exposure to the air or detonate on warming. An old preparation, or one that has been warmed with water for some time with a view to its purification, will not be so dangerous, but then it will contain much free metallic osmium. The estimation of osmium as dioxide is therefore untrustworthy (see A., 1910, ii, 305).

Stable Osmium Dioxide.—An amorphous oxide containing about 1% of sodium chloride may be obtained by heating potassium osmichloride with pure sodium hydroxide solution in the absence of air. The dried powder corresponds with the formula $OsO_2,2H_2O$. One molecule of water is lost at 100° and the other at 200°, the residue being a bluish-black powder, D^{21} 7·71. The reaction of this oxide with hydrogen is almost explosive in its violence. Oxygen also reacts briskly, giving osmium tetroxide. When heated in an indifferent atmosphere, it becomes dark brown and decomposes at about 500° into osmium and osmium tetroxide. In an atmosphere of osmium tetroxide, however (partial pressure about 100 mm.), it may be heated to 640°, when it changes into a crystalline form, D^{22} 7·91. A copper-coloured sublimate (octa-

hedra and hexahedra) is usually deposited on the tube, and it may be that the volatile oxide to which the formation of this sublimed dioxide is due is a trioxide, thus: $OsO_2 + OsO_4 \rightleftharpoons 2OsO_3$. The pure dioxide could be obtained by heating metallic osmium in an atmosphere of nitrogen and osmium tetroxide at 650°, but the pure metal must be as finely divided as possible. J. C. W.

Mineralogical Chemistry.

The Solvents of Coal. A. WAHL (*Bull. Soc. chim.*, 1917, [iv], **21**, 76—88).—An examination of the behaviour of different types of coal towards aniline and quinoline as solvents. The results obtained are in agreement with those of Vignon (compare A., 1914, ii, 570), Bedson (compare A., 1908, ii, 302), and Dennstedt and Bünz (compare *Zeitsch. angew. Chem.*, 1908, **21**, 1833). W. G.

Högbomite. AXEL GAVELIN (*Bull. Geol. Inst. Upsala*, **15**, 287—316; from *Chem. Zentr.*, 1917, i, 601).—The new mineral occurs in the iron ores in the neighbourhood of Ruoutevare (Lapland) associated with magnetite, ilmenite, pleonaste, corundum, and hydrargillite; it is hexagonal-rhombohedral, laminar, occasionally twinned toward the basis, very brittle, and conchoidal in fracture. The latter shows shining black, metallic particles which exhibit pleochroism similar to biotite. It is optically uniaxial, negative, and has ω 1·853, δ 1·803, hardness 6·5, D *ca.* 3·81. It is attacked by acids with difficulty, but, like pleonast and corundum, it is hydrated with loss of small amounts of TiO_2 and Fe_2O_3. Analysis (MAUZELIUS), after allowance for admixed ilmenite and pleonaste, gave:

TiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	MnO.	MgO.
5·33	61·19	17·41	0·29	0·14	15·44

This leads to the formula $RO,2R_2O_3$ if a portion of the R_2O_3 is replaced by TiO_2. Chemically, therefore, högbomite is a pleonaste in which the ferrous oxide is oxidised and partly replaced by titanium dioxide; in its physical properties it is most closely allied to the corundum–hæmatite group. H. W.

Leverrierite from Colorado. ESPER S. LARSEN and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1917, **7**, 208—217).—The determination of the composition and the physical properties of the "clay-gouge" which occurs in the veins of quartz and pyrolusite at Beidell, Saguache Co., Colorado, has shown that this belongs to the leverrierite group. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O. (<110°).	H_2O. (>110°).	Total.
47·56	20·57	8·58	0·24	2·52	0·80	1·28	trace	6·65	12·01	100·21

These results are compared with those obtained for rectorite, leverrierite from Rochelle (France), batchelorite, kryptotile, and delanouite. These minerals show some variation in the water content and in the $SiO_2:Al_2O_3$ ratio, but the optical properties indicate that they belong to the same group and are probably related to the micas. H. M. D.

Staurolite. Friedrich Hörner (*Jahrb. Min.*, 1917, i, *Ref.* 23—27; from *Inaug.-Diss., Heidelberg*, 1915, 41 pp.), E. A. Wülfing, and F. Hörner (from *Sitzungsber. Heidelberg, Akad. Wiss., Math.-naturw. Kl.*, 1915, 11 pp.).—Detailed determinations were made of the crystallographic, optical, and other constants of staurolite from Pizzo Forno, St. Gotthard ($a:b:c=0{\cdot}4734:1:0{\cdot}6820$; anal. I), Aschaffenburg, Bavaria (anal. II), and Petersdorf, Moravia (D 3·778). Staurolite is frequently rendered impure by the enclosure of quartz and other minerals, but the material analysed was quite pure. The analyses lead to the new formula $H_2O,4FeO,9Al_2O_3,8SiO_2$.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O (at 110°).	H_2O (110—1000°).	Total.	Sp. gr.
28·08	0·73	51·90	1·80	13·39	2·08	0·11	1·62	99·71	3·753
27·68	0·77	53·37	2·33	12·69	1·78	0·13	1·46	100·21*	3·759

* Also MnO, trace; CaO, nil.

L. J. S.

Scapolite-bearing Bombs from the Laacher See District. Refractive Indices of Sulphate-Scapolite. R. Brauns (*Jahrb. Min.*, 1917, i, 9—44).—A few more of the scapolite-bearing bombs are described in detail, and optical constants and analyses are given of the new member of the scapolite group, namely, sulphate-scapolite (A., 1915, ii, 836) or silvialite (R. Brauns, 1914). Analysis I is of colourless, transparent scapolite from a hornblende-scapolite-rock. This corresponds with $5[CaO,3CaAl_2Si_2O_8]$(meionite) + $4[CaSO_4,3CaAl_2Si_2O_8]$ (silvialite) + $2[CaCO_3,3CaAl_2Si_2O_8]$ (carbonate-meionite) + $2[NaCl,3NaAlSi_3O_8]$ (marialite) + $Na_2O,6NaAlSi_3O_8$ (chlorine-free marialite). Anal. II is of scapolite crystals from a felspar-hornblende-scapolite-rock, and corresponds with
$14[CaO,3CaAl_2Si_2O_8]+8[CaSO_4,3CaAl_2Si_2O_8]+5[Na_2O,6NaAlSi_3O_8]$; III of corroded scapolite from a hornblende-haüyne-scapolite-rock; and IV of the greyish-white grains of haüyne from the same rock; this agrees only approximately with the Brögger and Bäckström formula for haüyne, which is criticised. Analysis V is of the clear, fresh felspar from an anorthite-hornblende-scapolite-rock, and corresponds with $Ab_{15}An_{85}$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	SO_3.	Cl.	H_2O. at 100°.	H_2O. >110°.	Total.	Sp. gr.
I.	43·98	29·99	0·59	18·35	0·14	2·73	0·67	2·28	0·49	—	0·21	100·07*	2·755
II.	46·59	26·33	1·31	15·70	0·52	3·68	1·11	2·06	trace	0·80		98·10	2·748
III.	44·04	28·48	0·92	18·72	0·18	2·97	0·25	2·06	—	0·04	2·09	99·87†	2·755
IV.	32·41	27·65	0·06	10·11	0·07	13·30	1·85	11·88	0·38	0·40	1·60	99·97‡	2·45—2·46
V.	45·70	33·93	0·92	17·22	0·09	1·77	0·20	0·11	—	0·32		100·31§	2·746

* Also CO_2, 0·64; TiO_2, MnO, traces. † Also TiO_2, 0·12. ‡ Also FeO, 0·26.
§ Also MnO, 0·05; BaO, trace.

L. J. S.

History of Chinese Mineralogy and Chemical Technology. H. J. HOLGEN (*Chem. Weekblad*, 1917, **14**, 468—476).—An account of early records of Chinese scientific investigations, and their application to industry. A. J. W.

Analytical Chemistry.

Reducing Matter Extractable from Filter Paper. R. S. McBride and J. A. Scherrer (*J. Amer. Chem. Soc.*, 1917, **39**, 928—933).—The authors show that when solutions, to be estimated volumetrically by means of potassium permanganate, have to be filtered before titration, the results are somewhat high owing to the washing out of a reducing substance from the paper by means of the reagents. To ascertain the amount of this substance and the dimensions of the error introduced, a number of experiments have been made with various types of filter papers. The experiments were made by running quantities of various reagents of 250 c.c. in each case through the paper; the filtrate was then coloured with 0·03 c.c. of $N/10$-potassium permanganate, and the time required for the solution to become colourless compared with the time required in a blank. Solutions of sulphuric acid ($2\frac{1}{2}$ and 5%), sodium hydroxide (1%), and sodium carbonate (2%) were used. In every case, whether the solutions were filtered hot (70°) or cold, the permanganate is reduced much more rapidly than in the blank experiments. It is shown that a comparatively small volume of the reagent removes the reducing substance which is not reformed. Maceration of the paper with the reagent does not give any more of the reducing substance, even although the titration is carried out in the presence of the paper pulp. Old filter papers have just the same action as new ones. It is suggested that a preliminary washing of the filter paper with the reagent will remove all source of error. The reducing substance is probably furfuraldehyde.

J. F. S.

Improvement in the Use of the Gooch Crucible. Ernst Korten (*Chem. Zeit.*, 1917, **41**, 267).—The washing of precipitates in a Gooch crucible is facilitated by means of a glass, dome-shaped cover which is fixed on the crucible by a rubber band; a tube passes through the top of the cover and extends into the upper part of the crucible, the part of the tube above the cover being bent downwards and either connected with a wash-bottle or dipped into water contained in a beaker. The crucible is connected with a suction pump in the ordinary way, and the flow of water into the crucible is regulated by a tap and screw-clip. W. P. S.

Methyl-red [as an Indicator]. F. Lehmann and G. Wolff (*Arch. Pharm.*, 1917, **255**, 113—119).—Methyl-red (*p*-dimethyl-

aminoazobenzene-*o*-carboxylic acid) has about the same universal value as an indicator for the titration of bases of all strengths that phenolphthalein has for acids. That is, it is more sensitive to hydroxyl ions than is methyl-orange. It is also more sensitive towards hydrogen ions (compare Fels, A., 1910, ii, 320), and might therefore be of more extended use than methyl-orange in acidimetry, but probably of less use in the titration of salts of strong bases with weak acids. This has now been tested, and it is found that oxalic and picric acids can be titrated readily with it, and also alkali borates and cyanides, whilst sulphites do not give sharp end-points, and sulphides and carbonates give intermediate orange tones which should be ignored and the final change to bright pink waited for. The change from red (acid) to yellow (alkaline) is as sharp as the change from yellow to red, and solutions standardised against phenolphthalein are practically of the same normality with regard to methyl-red. The best results are obtained with two or three drops of a 0·1% solution in about 100 c.c. of liquid.

J. C. W.

Handling a Standard Solution of Barium Hydroxide. W. G. Haynes (*J. Ind. Eng. Chem.*, 1917, **9**, 58—59).—In order to avoid the use of rubber tubing to connect the syphon tube of the barium hydroxide reservoir with the burette, a glass valve may easily be constructed out of a T-tube and a glass rod of such thickness that it slides smoothly in the longer arm of the T. The latter is closed at one end to a small hole one or two millimetres in diameter, and the glass rod, rounded off, is ground into the partly closed end of the T-tube to make a tight joint. The syphon tube is then connected with the free arm of the T, the glass rod bent round twice at right angles and held in position by a weak spring, and the whole is fixed by means of a rubber stopper in the top of the burette. A slight upward pressure on the glass rod opens the aperture in the T-tube and allows the hydroxide solution to flow between the rod and the sides of the tube into the burette.

G. F. M.

Yellow Mercuric Oxide as a Standard in Alkalimetry. G. Incze (*Zeitsch. anal. Chem.*, 1917, **56**, 177—191).—Yellow mercuric oxide is readily prepared in a pure state, is anhydrous and non-hygroscopic, and is a trustworthy substance for use in standardising acid solutions, since it yields an equivalent quantity of alkali hydroxide when treated with potassium iodide: $HgO + 4KI + H_2O = K_2HgI_4 + 2KOH$. For use, a weighed quantity of about 0·4 gram of the oxide is mixed with 10 c.c. of 60% potassium iodide solution and, as soon as the oxide has dissolved, the mixture is titrated with the acid solution to be standardised, using methyl-orange, methyl-red, or phenolphthalein as the indicator.

W. P. S.

Valuation of Bromides. E. Rupp and E. Hollatz (*Arch. Pharm.*, 1917, **255**, 120—129).—The authors have developed a titrimetric method for the estimation of bromides in the presence

of small quantities of chlorides, which is designed especially for the valuation of pharmaceutical preparations, such as *Bromum compositum*, D.A.-B. ($KBr:NaBr:NH_4Br$, 2 : 2 : 1). The process is summarised in the following equations: $5KBr + KBrO_3 + 6H_2SO_4 = 3Br_2 + 6KHSO_4 + 3H_2O$; $Br_2 + 2NaOH + H_2O_2 = 2NaBr + O_2 + 2H_2O$; $KBrO_3 + 6KI + 6H_2SO_4 = 3I_2 + 6KHSO_4 + KBr + 3H_2O$.

The reason for removing the bromine by the application of alkaline hydrogen peroxide, rather than by boiling, is that the excess of bromate is not stable in hot acid solutions. Ammonium salts tend to produce bromates at this stage, however, so the first step is really to expel any ammonia by boiling with sodium hydroxide. The solution is then cooled, acidified, treated with a definite excess of bromate, then mixed with alkaline hydrogen peroxide, and, after boiling, acidifying, and adding potassium iodide, the iodine is titrated by thiosulphate. Sufficiently trustworthy results are obtained even if the mixture contains as much as 25% of a chloride.

J. C. W.

Estimation of Oxygen in Blood. D. D. VAN SLYKE (*Proc. Soc. Exp. Biol. and Med.*, New York, 1917, **14**, 84—85; from *Physiol. Abstr.*, 1917, **2**, 178).—The estimation can be made in five minutes by means of the author's apparatus for the estimation of carbon dioxide. After complete extraction of air from the apparatus and reagents, 2 c.c. of blood are laked with dilute ammonia solution and allyl alcohol. The oxygen is liberated by shaking with 0·5 c.c. of air-free, saturated potassium ferricyanide solution in a vacuum, and is estimated precisely as is carbon dioxide. The only correction needed is for the small amount of nitrogen gas present in blood.

G. B.

Estimation of Sulphur in Pyrites. C. ZAY (*Stat. sperim. agrar. ital.*, 1916, **49**, 530—536; from *Chem. Zentr.*, 1917, i, 446). —Finely powdered pyrites (1 gram) is treated in a covered porcelain dish with a cold mixture of nitric acid (20 c.c.) and concentrated hydrochloric acid (5 c.c.); when the reaction has subsided, the solution is evaporated to dryness, the residue moistened with hydrochloric acid (5 c.c.), again evaporated to dryness, and subsequently dissolved in a mixture of water (100 c.c.) and hydrochloric acid (1 c.c.). The iron is precipitated by ammonia (D 0·91, 10 c.c.) and the mixture warmed for ten minutes at 60—70°. The precipitate is filtered and the filtrate brought to 250 c.c. by washings of the precipitate (solution *A*). The ferric hydroxide is dissolved in the minimum quantity of concentrated hydrochloric acid, the solution diluted to about 175 c.c., the iron again precipitated, and the filtrate brought to 250 c.c. (solution *B*). One hundred c.c. of each of the solutions *A* and *B* are neutralised with dilute hydrochloric acid in the presence of methyl-orange and, after addition of hydrochloric acid (1 c.c.), precipitated at the boiling point with barium chloride solution (3%, 100 c.c.). After remaining for half an hour, the solution is decanted, the precipitate washed four times by decantation with boiling water (100 c.c.), filtered, and washed until

5 c.c. of the filtrate do not give a turbidity when mixed with 5 c.c. of dilute sulphuric acid. The precipitate is subsequently dried and ignited. H. W.

Estimation of Total Nitrogen. G. H. G. LAGERS (*Chem. Weekblad*, 1917, **14**, 492—499).—A comparative study of methods for estimating nitrogen in manures, including those of Kjeldahl, Schlœsing, and Jodlbaur, and the distillation method. A. J. W.

The Phenoldisulphonic Acid Method for Estimating Nitrates in Soils. CHARLES W. DAVIS (*J. Ind. Eng. Chem.*, 1917, **9**, 290—295).—The accuracy of the usual method of applying phenoldisulphonic acid for the estimation of nitrates in soils is not affected by the presence of ammonia in the atmosphere during the operation, or by the manner in which the acid is added, whether with or without stirring, or by the temperature of the solution at the time alkali is added to develop the colour, except that at 0° a loss (4 parts per million in a 100 part per 1,000,000 solution) was noted. Light, however, affects the colour, and the reading should be made without delay. Loss of nitrates was found to occur during the evaporation on the water-bath, notably when chlorides and sulphates were present, but carbonates, acetates, and salts of weak acids generally produced no accentuation of the loss. A maximum loss of 30% of the nitrate present was observed when uniform amounts of phenoldisulphonic acid were used with increasing proportions of nitrate. By evaporating the solutions to dryness with a slight excess of calcium hydroxide, all loss was prevented, even in the presence of chlorides and sulphates, provided that care was taken also to flood an excess of the sulphonic acid reagent quickly over the residue; otherwise the hydrochloric acid generated when chloride is present may lead to the escape of nitric acid. Potassium alum may be used as a flocculent in preparing the soil solution without causing loss of nitrate, provided the modified method of procedure is employed, and it is recommended as superior to copper sulphate and other flocculents for this particular purpose. G. F. M.

Estimation of Phosphorus in Zinc Phosphide. G. LIBERI (*Ann. Chim. Applicata*, 1917, **7**, 144—151).—The estimation of phosphorus in phosphides by oxidation to phosphate by means of nitric acid or aqua regia is not applicable to phosphides which are readily attackable by dilute hydrochloric or sulphuric acid, since with these the oxidation is only partial. This is the case with zinc phosphide, which, however, liberates its phosphorus quantitatively as hydrogen phosphide when treated with dilute sulphuric acid (1 vol. of the acid to 2 vols. of water). The method of estimation proposed by the author depends on this reaction, which is carried out in a current of carbon dioxide and occurs largely in the cold; when the reaction slackens, the liquid is gently boiled for half an hour, the flame being then extinguished and the carbon dioxide kept flowing for another half an hour. The hydrogen phosphide

formed is absorbed by 50 c.c. of a neutral 3% silver nitrate solution contained in a 7- or 10-bulbed tube, this being followed by a Péligot tube containing 10 c.c. of the solution, which serves as a check and should remain clear. The bulbed tube is emptied into a beaker together with the nitric acid and water used to rinse it out, and the whole gently heated on a water-bath until the precipitate completely dissolves. The silver is then precipitated with a slight excess of hydrochloric acid and the liquid evaporated almost to dryness, diluted again with water, filtered, and washed. In the filtrate the phosphoric acid is precipitated in the hot as ammonium magnesium phosphate and weighed after ignition as magnesium pyrophosphate. The result obtained in this way represents the active phosphorus.

If the total phosphorus, including that present in the phosphide as phosphate, is required, the following method may be used. The substance (0·2—0·3 gram) is introduced into a flask fitted with a tapped funnel and a delivery tube connected with a Péligot tube containing 10 c.c. of the 3% silver nitrate solution, the flask having been previously filled with carbon dioxide. About 10 c.c. of water are introduced through the funnel and then 50 c.c. of the silver nitrate solution, the flask being shaken. Nitric acid is next gradually added and the liquid heated until solution is complete, the flame being then extinguished and the current of carbon dioxide continued for fifteen minutes longer. The Péligot tube serves also in this case to indicate if there is any slight escape of hydrogen phosphide; if its contents show any brown coloration, they are subsequently added to the main liquid in the flask. Owing to the presence of dissolved zinc and silver, the phosphate must first be precipitated as ammonium phosphomolybdate.

Zinc phosphide should not contain more than very small proportions of arsenic. T. H. P.

Estimation of Phosphoric Acid and Phosphates by Alkalimetric Methods. JOHN H. SMITH (*J. Soc. Chem. Ind.*, 1917, **36**, 415—419).—Attempts to titrate solutions of phosphoric acid with *N*/1-sodium hydroxide at the ordinary temperature in the presence of methyl-orange, methyl-red, and phenolphthalein respectively show that the generally accepted points of neutrality with the first- and third-named indicators are only approximately correct; the end-points are, however, quite regular and fairly definite, so that correct results may be obtained by using certain factors. If the titrations are accomplished at 55°, however, accurate results are obtained without the use of factors.

For the analysis of phosphates, 5—6 grams of the sample are dissolved in the minimum quantity of distilled water and two drops of phenolphthalein are added; if the solution is not coloured pink, the absence of Na_3PO_4 and Na_2CO_3 may be assumed. The solution is heated to 55° and titrated at this temperature with *N*-sodium hydroxide solution until a pink coloration is noticeable. The determination of the end-point requires a certain amount of practice and is facilitated by the presence of sodium chloride. The

solution is next titrated back with N-hydrochloric acid with addition of a few drops of methyl-orange solution. Sufficient data are thus obtained if it is known that the solution contains only $Na_2HPO_4 + NaH_2PO_4$ or $NaH_2PO_4 + H_3PO_4$. In order to make the method uniform, however, the author prefers to add a further quantity of N-hydrochloric acid (about equal to that previously employed) to the solution, which is then boiled vigorously for at least fifteen minutes, whereby carbonates are decomposed and any metaphosphoric acid or metaphosphate is converted into the ortho-form; after being cooled to 55°, the excess of acid is neutralised by N-sodium hydroxide at first to the disappearance of the methyl-orange pink and finally to the appearance of the phenolphthalein pink. If now the last end-point corresponds with the original end-point, the possibility of the presence of metaphosphoric acid and its salts as well as of carbonates in the original substance is excluded. For full details with regard to calculations, the original memoir should be consulted.

When all precautions are taken, results within 0·5% of accuracy are obtained.

When metaphosphate is known to be present, N-sulphuric acid should replace N-hydrochloric acid and the solution should be evaporated to dryness after boiling to ensure the complete conversion of the meta- into the ortho-form; otherwise, however, it is preferable to employ hydrochloric acid. H. W.

Detection of Arsenic by means of Mercuric Chloride Paper. L. VUAFLART (*Ann. Falsif.*, 1916, **9**, 446—448).—The advantages of the Gutzeit test are discussed. As applied to certain samples of "glucose" containing large quantities of arsenic, the method gave higher but more trustworthy results than did the Marsh test. The interfering action of sulphites, which are sometimes present in "glucose," may be overcome by precipitating the arsenic as ammonium magnesium arsenate and then testing the precipitate. W. P. S.

Arsenic Trisulphide. ERNST SCHMIDT (*Arch. Pharm.*, 1917, **255**, 45—64).—A description of tests which have been made as to the behaviour of precipitated arsenious sulphide towards various liquids. It is found that the sulphide is appreciably decomposed by water and even by alcohol with formation of hydrogen sulphide. It is also attacked to a very considerable extent by dilute hydrochloric acid, but the action with dilute acid or with water is checked by the addition of a small quantity of hydrogen sulphide.

The estimation of arsenic by precipitation and weighing as trisulphide (Puller, this Journal, 1871, **24**, 971; Friedheim and Michaelis, A., 1896, ii, 74) gives results which are very slightly high, but actually the precipitate diverges more widely from the composition As_2S_3 than the errors would indicate, containing to some extent both arsenic hydrosulphide, $As(SH)_3$, and arsenious

oxide, the respective errors being in opposite directions and tending to equalise each other.

A slightly modified method is suggested for the treatment of precipitated arsenic sulphide in order to convert it into an arsenious solution suitable for titration with iodine. D. F. T.

Carbon Dioxide Absorption Apparatus. L. G. WESSON (*J. Ind. Eng. Chem.*, 1917, **9**, 59).—A new carbon dioxide absorption apparatus for organic combustions consists of a cylindrical bulb of thin glass containing moist soda-lime, connected near the base by means of a thick-walled capillary tube with a small vertical side-arm sufficiently large to hold about 7 grams of calcium chloride. Both necks of the apparatus are provided with ground-in stopcocks, and the whole when empty weighs only 20 to 25 grams. G. F. M.

Estimation of Carbon Dioxide in Water. J. TILLMANS and O. HEUBLEIN (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 289—304).—Free carbon dioxide and that present as hydrogen carbonates in water cannot be estimated accurately by precipitation with barium hydroxide and titration of the excess of the latter after the barium carbonate has settled; the inaccuracy of this method is due to the occlusion of barium hydroxide in the precipitated carbonate. The method is applicable, however, to solutions of carbon dioxide and hydrogen carbonates in distilled water provided that the whole mixture (liquid and precipitate) is titrated, using phenolphthalein as indicator; the presence of magnesium salts renders this modification useless in the case of many drinking waters. The free carbon dioxide in water may be estimated by adding 1 c.c. of 0·0375% phenolphthalein solution to 200 c.c. of the water contained in a stoppered flask and then titrating the solution with $N/20$-sodium hydroxide solution until a pink coloration is obtained which persists for five minutes. If, at the end of the titration, the solution contains more than 440 mg. of carbon dioxide in the form of hydrogen carbonate, the estimation must be repeated after the sample has been diluted with water free from carbon dioxide. Winkler's method (A., 1915, ii, 281) is considered to be untrustworthy. W. P. S.

Accurate Estimation of Silica in Commercial Analysis. F. G. HAWLEY (*Eng. and Min. J.*, 1917, **103**, 541—543; from *J. Soc. Chem. Ind.*, 1917, **36**, 521).—Attention is directed to sources of error in the estimation of silica due to the solubility of silica in hydrochloric acid, the presence of silica in the fusion mixture itself, and to impurities retained by the washed silica. The solubility of the silica, which may amount to 2% in samples containing less than 20% of silica, may be diminished by heating the saline residue at 150° during thirty minutes, then adding 15 c.c. of hydrochloric acid (60%), heating the mixture to boiling for three minutes, and collecting the silica on a filter, where it is washed successively with water, dilute hydrochloric acid, and water. To estimate silica

in ores containing much lead, copper, antimony, etc., the ore may be fused in a nickel crucible with a mixture of sodium hydroxide and sodium peroxide (equal parts by weight), followed by the above method of separation. Under these conditions, the loss of silica by solution is about 0·4%, but this loss is balanced approximately by impurities in the silica and the quantity of the latter derived from the fusion mixture. H. W.

Detection of Calcium in the Presence of Barium and Strontium. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 138—141).—The test described depends on the insolubility of calcium fluoride and the relative solubility of barium fluoride and strontium fluoride. One litre of water dissolves 16 mg. of calcium fluoride, 117 mg. of strontium fluoride, or 1630 mg. of barium fluoride. Barium fluoride solution is used as the reagent. A distinct turbidity is produced when this solution is added to 10 c.c. of water containing 0·0008 gram of calcium (as chloride). The presence of strontium chloride or ammonium chloride in the calcium chloride solution does not affect the sensitiveness of the reaction, but it is decreased when barium chloride is present. W. P. S.

Estimation of Zinc by Schaffner's Method. W. ORLIK (*Zeitsch. anal. Chem.*, 1917, **56**, 141—144).—A reply to Patek's criticism of this method (A., 1916, ii, 578). W. P. S.

Estimation of Zinc. J. H. HASTINGS (*Met. and Chem. Eng.*, 1917, **16**, 263—265; from *J. Soc. Chem. Ind.*, 1917, **36**, 506).—Solution of the ore and separation of iron and manganese are effected as usual, the zinc being determined by titration with standard potassium ferrocyanide in a boiling, slightly acid solution (volume about 200 c.c. containing 5 c.c. excess of hydrochloric acid) containing hydrogen sulphide, a saturated aqueous solution of which (50 c.c.) is added to prevent decomposition of the ferrocyanide by oxidising agents and to precipitate any small quantity of copper present. A solution of uranium nitrate (5%) is used as external indicator. H. W.

Analysis of Antimonial Lead. C. R. MCCABE (*J. Ind. Eng. Chem.*, 1917, **9**, 42—44).—The method adopted is that of Demorest (A., 1913, ii, 982), modified with the object of freeing the precipitate of lead sulphate from antimonial contamination. One gram of alloy is dissolved completely in 50 c.c. of concentrated sulphuric acid, finally boiling for five minutes to oxidise the tin. On dilution with water, lead sulphate is precipitated, and, after boiling, the precipitate is collected, dissolved in a 20% solution of ammonium acetate, and reprecipitated with sulphuric acid. It is then quite free from antimony, and may be collected on a Gooch crucible, and weighed. Antimony is determined in the two filtrates separately by titration with permanganate and ferrous sulphate, and tin in the first filtrate by the iron reduction and iodine titration method. G. F. M.

Electrolytic Analysis with Small Platinum Electrodes. F. A. Gooch and Matsusuke Kobayashi (*Amer. J. Sci.*, 1917, [iv], **43**, 391—396. Compare A., 1912, ii, 986).—Slight alterations are made in the apparatus described previously (*loc. cit.*), so that the small electrodes may be used with volumes of solution similar to those usually employed in electrolytic analysis. The rotating electrode consists of a piece of platinum gauze, 1—2 cm. square, into the central meshes of which is fused the tapered end of a lead-glass rod; a length of platinum wire is twisted round the glass rod and serves for making the electrical connexion. The stationary electrode is a strip of thin platinum foil, 5 cm. by 0·5 cm., welded to a connecting wire and suspended in a thin glass beaker of about 120 c.c. capacity. A small filtering tube, for collecting disengaged particles of deposited metal, is made by fusing the end of a lead-glass tube to a disk of platinum gauze and coating the disk with a layer of asbestos. The beaker, both electrodes, and the filtering tube are weighed together before use. The apparatus may be used for the estimation of copper, nickel, and lead. W. P. S.

Electroanalysis using Silvered Glass Basins in place of Platinum Cathodes. Jul. Gewecke (*Chem. Zeit.*, 1917, **41**, 297—298).—The silvered basins are prepared as follows. A glass basin of about 100 c.c. capacity has its inner surface ground (this is best effected by means of a sand-blast, but etching with hydrofluoric acid may be used, although the surface produced is sometimes irregular), the basin is then treated with hot sulphuric acid and potassium dichromate, sodium hydroxide, nitric acid, and water, and is next nearly filled with a mixture consisting of 100 c.c. of silver nitrate solution and 2 c.c. of 40% formaldehyde solution; the silver nitrate solution is prepared by dissolving 8·5 grams of silver nitrate in 100 c.c. of water, adding ammonia until the precipitate first formed is nearly dissolved, filtering the mixture, and diluting the filtrate to 1 litre. The formaldehyde is added immediately before the mixture is poured into the basin, and in about four minutes the silvering is completed; the basin is then emptied, washed with water and alcohol, and dried. The temperature of the silvering solution should not exceed 30°, or the silver coating will be unequal. A thin strip of platinum foil is now bent over the edge of the basin so that its lower edge touches the silver coating, and the basin is weighed. A vulcanite screw clip is used for connecting the platinum strip with the negative pole of the source of electricity; a platinum anode is employed. The apparatus may be used for the electrolytic estimation of copper, cadmium, zinc, nickel, and cobalt. W. P. S.

The Hydrogen Peroxide Reaction for Copper and the Hydrolytic State of Dilute Copper Sulphate Solutions. Friedrich Mayer and W. H. Schramm (*Zeitsch. anal. Chem.*, 1917, **56**, 129—138. Compare A., 1907, ii, 549; 1916, ii, 314).—A $N/10,000$-copper sulphate solution yields a distinct reaction with hydrogen peroxide, and even smaller quantities of the metal

can be detected. The addition of sodium hydrogen carbonate increases the sensitiveness of the reaction. It is shown that in very dilute copper solutions a portion of the copper is present as the hydrosol of copper oxide. W. P. S.

Analysis of Babbit Metal. J. C. Witt (*Philippine J. Sci.*, 1916, **11**, [*A*], 169—175).—The following methods are recommended for alloys having the composition: lead, 85—90%; antimony, 10—15%; tin, 0—5%; and copper, 0—1%. *Antimony.*—This metal may be estimated by a modification of Low's method (A., 1907, ii, 304); the alloy is dissolved in sulphuric acid, the solution boiled with the addition of hydrochloric acid, then cooled, diluted, and titrated with potassium permanganate solution. *Tin.*—The alloy is decomposed with sulphuric acid, the solution then diluted, heated with hydrochloric acid and steel turnings in a current of carbon dioxide, and, when all the turnings have dissolved, the mixture is cooled and titrated with $N/10$-iodine solution; the steel turnings used should be as free as possible from phosphorus. *Lead.*—The tin is first separated by treating the alloy with nitric acid, the lead is then precipitated as sulphate; this is collected, washed, dissolved in hot ammonium acetate solution, and the solution is titrated with ammonium molybdate solution, using tannin solution as an external indicator. The ammonium molybdate solution is standardised against pure lead under the same conditions. *Copper.*—The alloy is decomposed with nitric acid, then treated with an excess of ammonia, and the copper is estimated colorimetrically. *Iron and Zinc.*—The filtrate from the lead sulphate is heated, treated with hydrogen sulphide, and any precipitate which forms is separated by filtration; the solution is then oxidised by boiling with the addition of nitric acid and the iron is precipitated as hydroxide; the zinc is estimated in the filtrate from the ferric hydroxide. It is convenient to prepare a set of standard Babbit metals for use in standardising the reagents used in the analysis. W. P. S.

Analysis of Aluminium Dust. J. E. Clennell (*Eng. and Min. J.*, 1917, **103**, 496—499; from *J. Soc. Chem. Ind.*, 1917, **36**, 506).—The sample (1 gram) is dried at 100° until constant in weight and the loss reported as moisture. The dried material is treated with ether, the filtered extract being evaporated in a tared flask and the grease weighed. The residue from the extraction is transferred to a 300 c.c. flask and dissolved in dilute hydrochloric acid; the hot acid solution is filtered through the filter previously used into another flask and the filter washed with hot water. The insoluble residue is washed back and treated with nitric acid; this solution is passed through the same filter into a separate flask. The ignited, insoluble residue consists of silica mixed with some carbon which persistently resists ignition. It is fused with a small quantity of sodium peroxide and the silica separated as usual; this is calculated to silicon. The nitric acid filtrate is evaporated with sulphuric acid and added to the main hydrochloric acid filtrate.

This is precipitated with hydrogen sulphide and the precipitate digested with hot hydrochloric acid (50%) to separate copper and lead. The residual copper sulphide is dissolved in nitric acid and the copper titrated with cyanide. The lead solution is neutralised with ammonia, acidified with acetic acid, and precipitated with dichromate. The filtrate from the hydrogen sulphide precipitate is oxidised and treated with an excess of sodium hydroxide; the precipitate is dissolved and reprecipitated with ammonia; the filtrate from the ferric hydroxide is used for the estimation of magnesium. The alkaline filtrate containing aluminium and zinc is precipitated with sodium sulphide and the zinc sulphide estimated with $N/10$-iodine and thiosulphate. The aluminium may be roughly estimated by acidifying the last filtrate, expelling hydrogen sulphide by boiling, making up to 500 c.c., and titrating 100 c.c. with $N/1$-alkali first with methyl-orange, and then with phenolphthalein as indicator. The interval between the two end-points is proportional to the aluminium; the alkali is standardised against pure aluminium. Special methods for the separate estimation of the impurities are also described. H. W.

Micro-diagnosis of a Jadeite Chisel. ALOIS CATHREIN (*Jahrb. Min.*, 1917, 1, *Ref.* 20—22; from *Zeitschr. Ferdinandeums, Innsbruck*, 1915, [iii], **59**, 241—251).—The material of a pale green stone chisel, D 3·34, from Mt. Bondone, Trent, Tyrol, was identified as jadeite by the following method—called a 'micro-tachy-method,' being quick and applicable to small amounts of material. A small chip is crushed for the determination of the optical characters under the microscope. The same powder is afterwards used for determining the fusibility and flame coloration, the intensity and duration of the flame giving some idea of the percentage of sodium, etc. A 'volumetric' analysis performed in the wet way in narrow tubes of the same gauge gives, from the volumes of the various precipitates, an approximation to the quantitative composition. Silicates are decomposed by hydrofluoric acid, and the precipitates are separated and washed by decantation. Control experiments on known substances are performed when necessary.
L. J. S.

Stripping and Analysis of Galvanised Iron. GEORGE W. HEISE and AMANDO CLEMENTE (*Philippine J. Sci.*, 1916, **11**, [*A*], 135—146).—Separation of the zinc from the iron may be effected by phosphoric acid, sodium hydrogen sulphate, hydrochloric acid, or sulphuric acid; acetic acid may also be used, but the action is slow. Further, the separation can be made by means of solutions of certain lead, cadmium, copper, cobalt, chromium, and aluminium salts. Stripping and analysis can be effected by the electric current by making the galvanised plate the cathode in sulphuric acid solution, or the anode in concentrated alkali hydroxide solution, or in an oxidising solution (for example, sodium nitrate solution). In any of these methods, the amount of iron removed, together with the zinc from the plate, is mainly that con-

tained in the zinc–iron alloy present in the coating, and is not due to corrosion of the iron plate itself. W. P. S.

Testing of Galvanised Iron. J. C. Witt (*Philippine J. Sci.*, 1916, **11**, [*A*], 147—165).—The zinc coating on galvanised plates may be separated and its quantity estimated by immersing a piece of the plate, 15 cm. by 15 cm., for about ten minutes in hydrochloric acid (D 1·098) at 45°, and then re-weighing the plate after it has been washed and dried. The small quantity of iron which is dissolved by the acid may be estimated by titrating the solution with permanganate solution. Measurements of the solution-velocity of galvanised iron indicate that the system of zinc–iron alloys is very complex; from the solution–velocity time curves an approximate idea of the uniformity and purity of the zinc coating may be obtained. W. P. S.

Estimation of Chromium in Ferrochrome. Koch (*Stahl & Eisen*, 1916, **36**, 1093; from *Chem. Zentr.*, 1917, i, 532. Compare Herwig, this vol., ii, 104).—In the analysis of ferrochrome rich in chromium the author controls the permanganate titre with $N/10$-potassium dichromate and has up to the present observed no discrepancies with the titre calculated from the iron factor 0·3109. H. W.

Estimation of Chromium in Ferrochrome. G. Schumacher (*Stahl & Eisen*, 1916, **36**, 1093—1094; from *Chem. Zentr.*, 1917, i, 532. Compare Herwig, this vol., ii, 104).—In the estimation of chromium by Phillips's method, the author has also obtained too low results for the chromium titre according to the usual methods of calculation. The discrepancies are greater than those observed by Herwig. H. W.

Chemical Evaluation of Alkali Chromates and Dichromates. J. F. Sacher (*Farbenzeitung*, 1916, **22**, 213; from *Chem. Zentr.*, 1917, i, 693).—The following method is sufficiently accurate for technical purposes and permits the estimation of chromate in presence of dichromate. Potassium dichromate can be titrated with potassium hydroxide in the presence of phenolphthalein in accordance with the equation $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$. The titration can be performed without the indicator, since, at the neutral point, the colour of the solution changes from reddish-yellow to greenish-yellow. Potassium chromate can be estimated by titration with sulphuric acid according to the scheme $2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$; Congo-red can be used as indicator. H. W.

Detinning and Analysis of Tin Plate. George W. Heise and Amando Clemente (*Philippine J. Sci.*, 1916, **11**, [*A*], 191—199).—The tin coating is most satisfactorily separated from tin plate by means of an electric current, the plate being made the anode

in a 30% sodium nitrate solution; the iron plate is not attacked under these conditions. The tin may also be removed by immersing the plate in lead acetate solution rendered alkaline with sodium hydroxide. W. P. S.

A New Industrial Apparatus for the Estimation of Combustible Cases. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1917, **15**, 146—162. Compare this vol., ii, 266).—A critical survey of the effect of the experimental conditions on the accuracy of the results obtained with the author's eudiometer, and a comparison of these results with those derived by the aid of other types of apparatus. A. J. W.

The Estimation of Gasolene Vapour in Air. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1917, **9**, 142).—The apparent complete agreement in the figures obtained by Burrell and Robertson (A., 1915, ii, 184) for the estimation of gasolene vapour in air by the combustion and liquid air condensation methods is due in the case of the higher percentages to the approximate method of computing the results of the combustions. When high percentages of gasolene are present (that is, over 5 or 6%), combustion is incomplete and the figures obtained are considerably below the truth. G. F. M.

Approximate Estimation of Toluene and Benzene in Coal Tar Oils. GEORGE HARKER (*J. Roy. Soc. New South Wales*, 1916, **50**, 99—105).—The oil is distilled from an ordinary distillation flask, the fraction boiling below 170° is collected, washed with sulphuric acid and with sodium hydroxide solution, and then distilled at the rate of 1 drop per second from a round-bottomed flask fitted with a Young and Thomas five-section still-head. The volume of distillate collected below 95° is approximately equivalent to the amount of benzene present, and the distillate collected between 95° and 130° gives the amount of toluene. The quantities of benzene and toluene are then checked by adding to the residue in the flask quantities of pure benzene and toluene in accordance with the amounts found in the preliminary distillation, and redistilling this mixture. Any error in the first estimation is thus corrected. W. P. S.

Analysis of Light Oils [for Benzene, Toluene, and Xylene]. G. EGLOFF (*Met. and Chem. Eng.*, 1917, **16**, 259—263; from *J. Soc. Chem. Ind.*, 1917, **36**, 498—499).—The still consists of a copper flask of 4000 c.c. capacity, provided with a fractionating column 2·4 m. high and a condenser 0·6 m. long. The column is made up of six 0·3 m. and one 0·45 m. lengths of 18 mm. and one 0·15 m. length of 36 mm. iron pipe connected by suitable unions; it has a reflux tube (9 mm. diam.) which extends through the lowest section of the column to within 25 mm. of the bottom of the flask when the latter is screwed into position. The reflux tube communicates with the main column at intervals, and the different

sections of the column are separated by diaphragms of 30-mesh iron wire gauze, each of which supports an 0·2 m. column of glass rods 50 mm. long and 12 mm. in diameter. The head of the column is provided with a thermometer and pipe connected to the condenser. The heating burners and, if necessary, the column are screened from draughts. Experiments with known mixtures of benzene, toluene, and xylene, distilled at the rate of 2 drops per second, gave results in close agreement with the theoretical, the loss being very small. In the case of various commercial oils, a much better separation of benzene, toluene, and xylene was effected by a single distillation in this apparatus than by three successive fractionations with a standard Hempel column.

For analysis, the oil (2000 c.c.) contained in a vessel provided with a cooling coil and stirring apparatus, is agitated for about eighty minutes with sulphuric acid (200 c.c., 95%), added at the rate of about 1 drop per second, and the mixture left for thirty minutes; the acid sludge is then discharged and the remaining oil, now free from olefines, agitated for fifteen minutes with a solution of sodium hydroxide (6%) and allowed to remain for thirty minutes. After separation from the alkali sludge, the oil is distilled with live steam until the temperature reaches 180°. The oil is then separated from the distillate and, after thorough drying with calcium chloride, distilled in the apparatus described, the fractions boiling up to 95°, between 95° and 125°, and between 125° and 165° being collected, measured, and recorded as pure benzene, toluene, and solvent naphtha unless the specific gravities fall below 0·880, 0·871, and 0·870 respectively, when the presence of paraffins is indicated. In the latter case the proportion of paraffins present is calculated on the basis of the wide difference in specific gravity between paraffin and aromatic hydrocarbons distilling over the same range of temperature; alternatively, 10 c.c. of the fraction are agitated with 25 c.c. of a mixture of concentrated sulphuric acid (D 1·84, 2 parts) and fuming sulphuric acid (20% oleum, 1 part) in a stoppered, graduated cylinder and the volume of undissolved paraffins is read off. H. W.

Estimation of Xylene in Solvent Naphtha. PERCY E. SPIELMANN and F. B. JONES (*J. Soc. Chem. Ind.*, 1917, **36**, 489—490).—This estimation is complicated by the fact that the xylene itself consists of three isomerides differing in b. p. and sp. gr., and that it exists as such in a complex mixture of cumene, trimethylbenzenes, and other substances which boil gradually up to 170° and over. The following procedure is recommended. Solvent naphtha (100 c.c.—or 200 c.c. if necessary for Colman's analysis) is distilled over a Young 12-pear head at the usual rate of 1 drop per second. The fractions up to 138° and from 138—170° (all temperatures being corrected) are collected in separate cylinders and measured. The benzene, toluene, and xylene in the first fractions (up to 138°) are estimated by Colman's methods for examining toluenes and solvent naphtha. The xylene in the 138—170° fraction is evaluated by determining the boiling

point in a constant boiling-point apparatus, such as that due to Northall-Laurie (A., 1915, ii, 704) and reference to a graph obtained by observation of the b. p. of known mixtures of xylene and residue, b. p. 143—170°. The accuracy of the boiling-point curve may be taken as ±1·5% when the xylene content of the fraction is above 50%.

For the estimation of paraffin, 100 c.c. of the sample is distilled over a Young 12-pear head at the rate of 1 drop per second, the portion distilling between 138° and 143° (corr.) being collected separately. Ten to 20 c.c. of this fraction are vigorously shaken for about forty minutes with two and a-half times the volume of weak oleum made by mixing one volume of 22% oleum with two volumes of 95% sulphuric acid. The absorption of the aromatic hydrocarbons is effected in a 100 c.c. flask, the neck of which is graduated into 10 c.c. and subdivided into tenths of a c.c. from the volume mark upwards. After sufficient shaking, the level of the liquid is driven up into the graduated neck by the addition of a further quantity of 95% sulphuric acid. After being allowed to remain, preferably overnight, the paraffin layer is found to be sharply separated. H. W.

Stannous Chloride Reduction Method for Estimating Nitrotoluenes. E. DE W. S. COLVER and E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1917, **36**, 480—483).—The authors have investigated the applicability of the methods of Knecht and Hibbert and of Altmann (A., 1901, ii, 475; reduction by stannous chloride and estimation of unused stannous salt by titration with iodine in alkaline tartrate solution) to the estimation of nitrotoluenes. With the latter method, it is essential to effect the reduction at 100°. The following method is, however, more convenient. The sample is placed in a 100 c.c. flask together with stannous chloride solution (2—2·5*N*, 20 c.c.) and concentrated hydrochloric acid (about 3 c.c.). The flask is then placed in boiling water and shaken, a blank experiment being performed at the same time. After being cooled and made up to 100 c.c., the blank and sample are diluted with water and titrated with iodine at the rate of about 2 drops per second. It is preferable to take the mean of several titrations. It is important to add the iodine at about the same rate to sample and blank, since it is found that in both cases the iodine required was less for a slow titration than for a quick one. If the iodine is added in a continuous stream to the pure stannous solution, the results of the acid titration agree most closely with those of the alkaline tartrate titration. The method has been applied to mono-, di-, and tri-nitrotoluenes, but the results are uniformly somewhat low, owing to a cause which has not yet been elucidated. The primary object of the investigation, however, was to find whether sufficiently constant numbers could be obtained to allow a calculation of the percentage composition of binary mixtures, and direct experiment shows that this can be accomplished with a very considerable degree of accuracy.

H. W.

Wet Combustion in the Nitrosite Combustion Method for the Direct Estimation of Caoutchouc. L. G. WESSON and E. S. KNORR (*J. Ind. Eng. Chem.*, 1917, **9**, 139—140. Compare A., 1913, ii, 631; 1914, ii, 593).—The method previousy described for the estimation of caoutchouc is simplified by a wet combustion of the nitrosite. The procedure is as follows. Half a gram of the finely divided sample is extracted for three hours with acetone and half an hour with chloroform, and the extracted sample is allowed to dissolve in or thoroughly absorb chloroform, and treated with nitrous acid until the green colour is permanent for fifteen minutes. After keeping overnight the chloroform is decanted through a dry Gooch crucible into the combustion flask; the chloroform is removed from both residue and filtrate by heating on a water-bath in a current of dry air. The residue is then extracted repeatedly with dry ethyl acetate and the liquid decanted through the Gooch crucible into the combustion flask until the filtered extract is colourless. After evaporation of the ethyl acetate the residue in the flask is heated on a water-bath for fifteen minutes and freed from solvent by adding 15 c.c. of water containing 1 drop of hydrochloric acid and rapidly evaporating once more to dryness in a calcium chloride bath in a current of air. The dry residue remaining in the flask is then burnt by means of sulphuric acid and potassium dichromate, collecting the products in a series of U-tubes containing calcium chloride and soda-lime. The weight of carbon dioxide obtained multiplied by the factor $(136 \times 200)/440$ gives the percentage of $C_{10}H_{16}$ in the sample. G. F. M.

Detection and Estimation of Small Amounts of Methyl Alcohol. ELIAS ELVOVE (*J. Ind. Eng. Chem.*, 1917, **9**, 295—297). —The colorimetric estimation of methyl alcohol by Simmonds's application (A., 1912, ii, 208) of Denigès's qualitative test is rendered much more sensitive by reducing the proportion of ethyl alcohol present from 10 to 0·5%, when as little as 0·1 mg. of methyl alcohol in 5 c.c. showed a coloration after forty minutes, after treatment with 2·5 c.c. of 2% permanganate and 0·2 c.c. of concentrated sulphuric acid, decolorisation of the excess permanganate after three minutes with 0·7 c.c. of 10% oxalic acid, further acidification with 1 c.c. of concentrated sulphuric acid, and the addition when cold of 5 c.c. of Schiff's reagent. The correct preparation of the Schiff's reagent is of importance, and the following procedure is recommended. 0·2 Gram of finely powdered magenta is dissolved in 120 c.c. of hot water; 2 grams of anhydrous sodium sulphite dissolved in 20 c.c. of water are added to the cold magenta solution, followed by 2·0 c.c. of hydrochloric acid (D 1·19) and water to make 200 c.c. After keeping for an hour, the reagent is ready for use. It should be made up fresh every week. G. F. M.

Modification of Fehling's Method of Sugar Estimation. EMIL LENK (*Deutsch. med. Woch.*, 1917, **43**, 43—44).—One mg.

of magnesium sulphate added to each c.c. of the copper sulphate solution ensures rapid sedimentation of the colloidal cuprous oxide. Calcium salts are harmful in this respect. For the estimation in urine containing less than 1 per cent. of dextrose, it is necessary to remove certain colloids by shaking for half a minute with a little blood charcoal and filtering once or twice through the same filter. On adding the urine drop by drop to boiling Fehling's solution containing magnesium, the cuprous oxide suddenly cakes together and the next drop makes the solution perfectly clear; this point corresponds with the disappearance of copper from the solution, and is therefore the true end-point. G. B.

Estimation of Sugar in Urine. L. VANINO and F. BERTELE (*Arch. Pharm.*, 1917, **255**, 134—139).—The authors have revived an almost forgotten method of the French physician, Duhomme (1874), and find it suitable for clinical purposes. Two c.c. of Fehling's solution are diluted with an equal volume of water in a series of tubes, and successive quantities of urine are counted by drops into the boiling reagent. The number of drops (x) necessary for reduction is then found by inspection. The apparatus is also tested in order to find how many drops go to make 1 c.c. (y; should be about 20—25). As 2 c.c. of Fehling's solution are reduced by 1 c.c. of 1% dextrose, y/x gives the percentage of sugar in the urine. J. C. W.

Influence of Amino-acids and of *l*-Glutimic Acid in the Estimation of Raffinose and Sucrose in Molasses by the Inversion Method. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1916, **41**, 154—160).—The presence of glutamic or *l*-glutimic acid diminishes the amount of sucrose found in all cases in which the ordinary methods of estimation are employed, only acid polarisation and the Clerget–Herzfeld formula giving accurate results.

Aspartic acid increases the amount of sucrose given by ordinary direct polarisation or by inversion and polarisation. Acid polarisation gives correct results if the Clerget–Herzfeld formula is used, but the raffinose formula gives low numbers.

In presence of aspartic or glutamic acid a positive amount, and in presence of *l*-glutimic acid a negative amount, of raffinose is indicated when this sugar is absent; the errors thus incurred are halved when acid polarisation is used.

With pure beet molasses it is well to discard the raffinose formula entirely and to determine the sugar content by the acid polarisation method and application of the Clerget–Herzfeld formula.

No method is known by which raffinose may be estimated in presence of amino-acids. T. H. P.

Direct Method for the Estimation of Starch. TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1916, **7**, 369—383; from *Chem. Zentr.*, 1917, i, 450—451).—The method depends on the solubility of starch in calcium chloride solution, its precipitation by iodine, and the decomposition of the precipitate by

alcohol. From 0·3 to 1·0 gram of the finely-divided, fat-free substance under examination is moistened with water and mixed with 20 c.c. of 50% calcium chloride solution; the mixture is heated in a boiling water-bath for thirty minutes, then boiled for five minutes, cooled, diluted to 100 c.c., and filtered through cotton-wool and then through asbestos. If the filtrate is not perfectly clear, it must be submitted to centrifugal action. Fifty c.c. of the filtrate are now treated with $N/50$-iodine solution until a flocculent precipitate is obtained, but a large excess of iodine is to be avoided. After about twenty-four hours a quantity of asbestos is added, the precipitate and asbestos are collected in a Gooch crucible containing a layer of asbestos, and the contents of the crucible are washed four times with 5% calcium chloride solution containing a few drops of iodine solution. The precipitate is then washed with 60% alcohol (this is allowed to act on the precipitate for five minutes), then with 85% alcohol, and finally with 100 c.c. of 90% alcohol. If the contents of the crucible are not now colourless, a quantity of hot alcohol is added. After further washing with cold 95% alcohol, 5% calcium chloride solution, and dry ether, the crucible and its contents are dried, weighed, ignited, and re-weighed. The loss in weight gives the quantity of starch present.

W. P. S.

Detection and Estimation of Formic Acid in Meat Extract. ERNST WASER (*Zeitsch. physiol. Chem.*, 1917, **99**, 67—85).—For the detection of formic acid, the meat extract is subjected to steam distillation and the distillate, after reduction with magnesium and hydrochloric acid, tested for formaldehyde. The quantitative estimation is performed with 10—20 grams of the extract, which is mixed with 100 c.c. of water and 30 to 60 c.c. of 6% phosphoric acid and distilled with steam; about 1500 c.c. of distillate are collected and the amount of formic acid present estimated by Fincke's method (A., 1913, ii, 636).

Meat extracts prepared from fresh meat contain about 0·5% of formic acid calculated on the dry extract. Formic acid is present in fresh meat, and increases in amount during putrefaction. Extracts prepared from putrescent meat may contain more than 1% of formic acid.

Hehner's test for formaldehyde in milk succeeds best when the concentration of formaldehyde lies between 1:300 and 1:20,000.

H. W. B.

New Qualitative Test and Colorimetric Method for the Estimation of Vanillin. CLARENCE ESTES (*J. Ind. Eng. Chem.*, 1917, **9**, 142—144).—Aqueous solutions of vanillin give a violet to violet-red coloration with an acid mercuric nitrate reagent after warming in boiling water for five minutes. The reagent is prepared by dissolving mercury in twice its weight of nitric acid (D 1·42) and diluting with twenty-five times the weight of water. It appears to be specific for vanillin, and can be utilised for the colorimetric estimation of this substance. In this case 5 c.c. of

standard 1% aqueous vanillin solution are treated with 0·5 c.c. of the reagent, placed in boiling water for ten minutes for the development of the maximum coloration, and, after cooling, diluted to 50 c.c. with water. The unknown solution is treated in exactly the same way, unless it is a vanilla extract, in which case, since the mercuric nitrate causes the precipitation of resins and colouring matter, an excess must be used, namely, 1·5 c.c., with an alcoholic extract, or 1 c.c. with an aqueous extract, and after the development of the colour the solution is made up to 50 c.c., filtered, and compared with the standard. G. F. M.

The Possibility of Titrating Mono-substituted Amino-groups of Amino-acids and Formaldehyde. A. CLEMENTI (*Arch. ital. de biol.*, 1915, published 1916, **64**, 332—340; from *Physiol. Abstr.*, 1917, **2**, 102).—Imino-groups, for example, that of sarcosine, react in Sörensen's formaldehyde titration according to the equation $2NHRR' + CH_2O = CH_2(NRR')_2 + H_2O$. G. B.

Method for the Identification of Phenylalanine-Carbamido-acid in the presence of Urea and Amino-acid. ALICE ROHDE (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxvii—xxviii; *J. Biol. Chem.*, 1917, **29**).—The urea is first decomposed by urease. After extraction of the urea-free material with ethyl acetate, the aqueous residues left on distillation with steam are analysed for traces of carbamido-acid by the gasometric method for the estimation of amino-nitrogen. Approximately quantitative results are obtained by this method when applied to urine containing known amounts of phenylalanine-carbamido-acid [α-carbamido-β-phenyl-propionic acid]. H. W. B.

Detection of Cryogenine in Urine. L. GRIMBERT (*J. Pharm. Chim.*, 1917, [vii], 305—306).—Cryogenine (*m*-benzamidosemi-carbazide), when rendered ammoniacal and exposed to air for twenty-four hours, is oxidised gradually and the solution becomes deep yellow in colour; the yellow colour is destroyed by the addition of sulphuric acid. If the acid solution is now shaken with ether, the ethereal solution separated and shaken with ammonia, the latter is coloured yellow. The substance may be detected in urine by rendering the latter alkaline, adding basic lead acetate, filtering the mixture, treating the filtrate with sulphuric acid, separating the lead sulphate, and then shaking the acid solution with ether. The ethereal layer is drawn off and shaken with ammonia; the alkaline aqueous layer is coloured more or less yellow, according to the quantity of cryogenine present. Oxidation of cryogenine evidently takes place in the body after administration. W. P. S.

The Estimation of Antipyrine. J. BOUGAULT (*J. Pharm. Chim.*, 1917, [vii], **15**, 337—339. Compare François, this vol., ii, 226).—The author has slightly modified his original method for the estimation of antipyrine by its conversion into iodoantipyrine (compare A., 1900, i, 312). W. G.

Sodium Perchlorate as a General Reagent in Microchemistry. G. Denigès (*Bull. Soc. Pharm. Bordeaux*, 1917, **5**; from *J. Pharm. Chim.*, 1917, [vii], **15**, 322—323).—Crystals, which in some cases are characteristic, are obtained when sodium perchlorate is added to alkaloid salts in dilute solution. For instance, a 0·2% brucine solution yields hexagonal plates or rhombic octahedra, whilst a 0·1% strychnine solution gives long, needle-shaped crystals. Cocaine (A., 1915, ii, 74), berberine, narceine, cotarnine, and papaverine also yield crystals when treated with sodium perchlorate, whilst veratrine and narcotine give amorphous precipitates. W. P. S.

Microchemical Precipitation of Alkaloids with Zinc Chloride-Iodine Solution. O. Tunmann (*Apoth. Zeit.*, 1917, **62**, 76—78; from *Chem. Zentr.*, 1917, i, 701—702).—The results were obtained with more or less impure alkaloid residues, such as are prepared by the Stas-Otto method. The reagent does not yield crystalline products with arecoline, brucine, cocaine, quinine, cinchonine, coniine, colchicine, narceine, nicotine, eserine, or veratrine. On the other hand, it is well adapted for the identification of strychnine, sparteine, the opium alkaloids, morphine, papaverine, cryptopine, and codeine, as well as atropine and hyoscyamine. With atropine, brown or dark red to blackish-red crystals, mostly rhombs, are immediately produced, which, at the commencement of the reaction, vary greatly in size. All the crystals shine but little between crossed Nicols, and do not exhibit pleochroism. The crystal crosses, consisting of four rhombs, are particularly characteristic. The limit of sensitiveness is 10—20 μg. The iodide crystals of hyoscyamine shine feebly in polarised light; they are very small (4—8 μ), almost black, and without pleochroism. The platelets have generally a far less regular circumference than the atropine crystals. Limit of sensitiveness, 10 μg. Zinc chloride-iodine yields crystals even with very impure morphine preparations; initially, fine, pale brown needles are formed, which after ten to twenty minutes unite to sheaves, and are then transformed into prismatic crystals with direct extinction. The latter are brown, the larger ones being nearly black; they do not exhibit pleochroism and scarcely shine between crossed Nicols. Limit of sensitiveness, 5 μg.

Papaverine and cryptopine give long, dull red, yellowish-red, or greenish-red crystals from 2—3 μ diameter which have direct extinction, show red to blue polarisation colours, and exhibit pleochroism. The latter phenomenon yields an excellent method of differentiating between the three opium alkaloids considered here. Limit of sensitiveness, about 10 μg. In addition to the crystals described above, deep red drops are also formed which, after some hours, pass into deep red aggregates; this points to the presence of a second alkaloid (? cryptopine) in papaverine.

Codeine behaves very differently. A powdery precipitate is first obtained, which when warmed deposits larger and smaller particles, from which very slender, generally curved, pale brown

crystals grow. The limit of sensitiveness is about 40 μg. Excess of the reagent is to be avoided. Sparteine is preferably converted into the sulphate, and this gives with the reagent fine, yellowish-red crystal threads, which form sheaves and brushes at their ends. When warmed, coarser prismatic crystals appear after about thirty minutes, and in addition, when further heated, yellow aggregates are occasionally obtained. All the crystals shine strongly in polarised light, have extinction parallel to the long axis, and show very marked pleochroism. When warmed with zinc chloride–iodine, strychnine gives brownish-red or blackish-red spheres or aggregates which attain a diameter of 50 μ, and lie separately or are grouped in chains. They glow red between crossed Nicols, but do not exhibit pleochroism. Limit of sensitiveness, 15 μg.

Unless specific mention to the contrary is made, the above data refer to the crystals which are produced after one to two hours' action. H. W.

Detection of Atropine and Related Mydriatic Alkaloids. R. EDER (*Schweiz. Apoth. Zeit.*, **54**, 501—504, 517—520, 534—537, 544—548, 560—563, 609—612, 621—624, 657—661, 669—670, 685—687, 717—719; from *Chem. Zentr.*, 1917, i, 448—500).—The methods employed in the detection of atropine and related mydriatic alkaloids are critically reviewed, and two new reagents for the detection and differentiation of the more important of these bases are described.

Bromine water and bromine–potassium bromide are recommended as reagents for the microchemical detection of the *Solanaceae* bases. A drop of the solution of the alkaloid in *N*/2-sulphuric acid is brought on to an object-glass, and a drop of the reagent is added; after a short time, with small magnification, a fine turbidity appears, followed more or less rapidly by the formation of minute crystals, which present the appearance of fine, pale yellow needles. The crystals rapidly increase and sink to the bottom of the liquid, which gradually becomes clear. In the inner portions, individual needles frequently grow to stout, yellow rods; at the edge of the drop, on the other hand, the needles speedily begin to disappear, whilst the solution becomes colourless. The crystals also disappear more or less rapidly from the inner portions, and the solution becomes colourless as the bromine evaporates. The shape of the crystals is best studied with a 180—250 times magnification, and the solution should be protected with a cover-glass, thus rendering the crystals more stable. They are fully described and figured in the original. The reaction of atropine towards bromine water has the advantage over other atropine reactions that it can be repeated as often as desired with one and the same specimen. When the solution has become clear and colourless, the characteristic precipitate can be again obtained by renewed application of bromine water. The reaction is distinctly obtained at dilution of 1 in 3000. The macrochemical behaviour of atropine in *N*/2-sulphuric acid solution towards bromine–potassium bromide [Br (1 gram), KBr (2 grams), water

(20 grams)] is similar to its action on bromine water, but the reaction is considerably more sensitive.

Hyoscyamine reacts with bromine water in much the same manner as atropine. The yellow, cloudy precipitate rapidly becomes crystalline, and disappears as the bromine evaporates. The highly magnified crystals, however, have a very variable character. For this reason, bromine water is a less suitable reagent for the detection of the alkaloid than bromine–potassium bromide. The limit of sensitiveness of the latter is reached at a dilution of about 1 in 5000. By means of the reaction, atropine can be detected in the presence of hyoscyamine in a mixture of the alkaloids.

The macrochemical behaviour of homatropine and scopolamine towards bromine water and bromine–potassium bromide exactly resembles that of atropine. The yellow precipitate obtained from scopolamine with bromine water appears under the microscope to consist exclusively of amorphous drops, crystallisation only occurring infrequently and at isolated points. Similar results are observed with bromine–potassium bromide. The precipitate of homatropine with bromine water is at first amorphous, but rapidly becomes crystalline, whilst that with bromine–potassium bromide closely resembles the precipitate with atropine.

With the exception of caffeine, the remaining alkaloids, which yield yellow or otherwise coloured precipitates with bromine water or bromine–potassium bromide, give only amorphous deposits. The crystalline compound from caffeine may be useful in the detection of the latter. Iodine–potassium iodide gives reddish-brown, crystalline precipitates with atropine, hyoscyamine, and homatropine, which are less characteristic than the bromine–potassium bromide compounds. With scopolamine, as with most other alkaloids, the precipitates are amorphous. Labile bromine additive compounds which readily lose bromine are probably formed from the two reagents described above and the mydriatic alkaloids.

With regard to the detection of atropine and related alkaloids, the author draws the following conclusions. There is no single reaction on which dependence can be placed for the detection of these substances. Of the many reactions which have been previously proposed, only a few are suited to the practical detection of the bases. The following are to be recommended: physiological examination, Vitali's reaction, behaviour towards concentrated sulphuric acid in the cold (no coloration) and in the warm (odour after addition of water). Of colour reactions, with the exception of the negative tests with Froehde's and Erdmann's reagent, only Wasicky's reaction with dimethylaminobenzaldehyde and, possibly, Arnold's reaction need to be considered. Among microchemical methods and reactions, micro-sublimation, the iodine–atropine salt, and, particularly, the reactions with bromine water and bromine–potassium bromide, give good results. In the presence of other alkaloids which give amorphous precipitates with the bromine reagents, a separation is necessary which can frequently be effected by micro-sublimation. H. W.

Distillation of Nicotine with Steam. HANS BREZINA (*Fachl. Mitt. österr. Tabakregie*, 1916, 3 pp.; from *Chem. Zentr.*, 1917, i, 700—701).—With the object of obtaining a greater concentration of nicotine in the vapour without employing the salting-out method, the author passes a current of steam through a series of flasks containing a solution of nicotine; each flask is heated at 102°. In this manner, the steam can be caused to contain as much as 4% of nicotine, and considerable economy is effected in the time of distillation. Complete removal of nicotine from its solutions cannot be effected by this means, but the method yields the maximum effect in a shortened time. H. W.

Estimation of Theobromine. LÉON DÉBOURDEAUX (*J. Pharm. Chim.*, 1917, [vii], **15**, 306—311).—The theobromine obtained from cocoa by Maupy's method (A., 1897, ii, 531) contains from 6 to 12% of impurity, and the author suggests the following alterations in the process with the object of separating the alkaloid in a pure state. One hundred grams of the cocoa are mixed with 40 grams of water and boiled for two hours with a mixture of 60 grams of phenol and 340 grams of chloroform; the liquid portion is then separated and the residue extracted twice with chloroform containing phenol, the mixture being boiled for one hour in each extraction. After filtration, the extracts are distilled to remove the chloroform, the residue is mixed with 900 grams of ether, and, after about eighteen hours, the precipitated theobromine is collected, washed with ether, then dissolved in warm dilute sulphuric acid (20 grams of sulphuric acid and 180 grams of water), and the solution is filtered into a flask containing 250 c.c. of ammonia; the ammoniacal solution is treated with 2 grams of silver nitrate, then evaporated until all free ammonia has been expelled, diluted to 500 c.c., and the precipitated silver–theobromine compound collected after twenty-four hours. The precipitate is washed with 250 c.c. of water, then mixed with water, decomposed with hydrogen sulphide, 600 grams of amyl alcohol are added to the mixture, and the whole is distilled until 200 c.c. of distillate (water plus amyl alcohol) have been collected. The residual amyl alcohol solution is filtered, kept at 15° for thirty-six hours, the crystallised theobromine then collected, washed with ether, dried at 100°, and weighed. The weight of the amyl alcohol filtered from the crystals should be noted; 1000 grams of amyl alcohol at 15° dissolve 0·200 gram of theobromine, and a corresponding correction is applied to the weight of theobromine obtained. W. P. S.

General and Physical Chemistry.

Molecular Refractivities of Certain Elements and Simple Compounds. GERVAISE LE BAS (*Chem. News*, 1917, **115**, 277—278).—A discussion of the refractivities of simple oxygen and nitrogen compounds with reference to the augmentation supposed to be due to unsaturation. H. M. D.

Measurements in the Short-waved Portion of the Arc Spectrum of Vanadium. WILHELM LUDWIG (*Zeitsch. wiss. Photochem.*, 1917, **16**, 157—185).—A detailed record of wave-lengths of lines in the arc spectrum of vanadium from λ 2207 to λ 4646. The relative intensities of the lines are indicated and the numbers compared with those given by previous observers.
H. M. D.

Quantitative Light-filter for the Ultra-violet Part of the Spectrum. N. P. PESKOV (*J. Physical Chem.*, 1917, **21**, 382—401).—It has been found that a gaseous mixture of chlorine and bromine may be advantageously used as a light-filter for the region $\lambda = 500$ to $220 \mu\mu$. By a modification of Henri's photographic method, the author has determined the absorption-coefficients of gaseous chlorine and bromine for forty-three lines of the ultra-violet spectrum emitted by an arc between iron and copper electrodes. The absorption of mixtures of the two gases satisfies the requirements of Beer's law. The distribution of radiant energy in the light transmitted by various mixtures has been determined. H. M. D.

Colour and Chemical Constitution. Quantitative Study of the Phthaleins and of other Fuchsone Derivatives. JAMES MOIR (*Roy. Soc. South Africa*, 1917).—Wave-length measurements of the absorption bands have been made for a series of about fifty derivatives of phenolphthalein and fluorescein in alkaline solution, and also when dissolved in concentrated sulphuric acid. The results lead to the conclusion that the change of colour which accompanies substitution is mainly due to the change in volume which is caused by the entry of the substituent element or group, the effect being more pronounced when the substitution occurs in the vicinity of the quinonoid linking.

In alkaline solution, the absorption bands of the derivatives of phenolphthalein are all displaced towards the region of greater wave-lengths as compared with the band of the parent substance. The magnitude of the displacement increases with the volume of the substituting element or group. Substitution in the meta-position produces an effect which is usually about twice as great as that produced by the same substitution in the ortho-position. Substitution in the phthalic ring has comparatively little influence

on the colour. Derivatives of fluorescein show the same relations as phenolphthalein derivatives, but it is to be noted that the oxo-linking in fluorescein is exceptional in its influence in that the band is displaced towards the region of shorter wave-lengths as compared with the phenolphthalein band.

In concentrated sulphuric acid solution, the colour is about five times as intense as that of the same substance in alkaline solution, and in all cases there is a difference in colour, the wave-length being shorter in the sulphuric acid solution. The wave-length data show the existence of a connexion between the wave-lengths of the bands for a particular substance in alkaline solution on the one hand and in sulphuric acid solution on the other.

If λ is the wave-length of the absorption band in alkaline solution and λ_1 the wave-length in sulphuric acid, then the relation between λ and λ_1 may be expressed by the equation $1/\lambda_1 = 3/2\lambda - c$, where c is a constant. The constant in the equation is supposed to represent the effect produced by combination of the substance with sulphuric acid, and it is suggested that the influence in question may be due to the formation of a ring structure in which the two phenolic hydroxyls are joined up by the sulphuric acid. The phenol rings thus form a part of the complex ring structure and occupy the same relative position as in fluorescein. H. M. D.

Absorption of X-rays. TYCHO E:SON AURÉN (*Phil. Mag.*, 1917, [vi], **33**, 471—487).—From a review of existing determinations, it appears that the ratio of the absorption-coefficients of two materials must be independent of the wave-length of the *X*-rays outside of the range of wave-length wherein selective absorption occurs and for rays of not too great wave-length. A new method, based on this, is described for accurately determining the absorption-coefficient of any element relative to that of water, for the most part by experiments on aqueous solutions of the salts of the element in question. The absorption of the solution of known concentration, considered as additively determined by the absorption of its constituent atoms, is accurately balanced by varying the thickness of the solution traversed against that of a standard water cell. Two ionisation chambers opposed to one another are used, and the current adjusted to zero by varying the thickness of the solution layer. The relative molecular absorption-coefficient, in terms of that of water as unity, is independent of the concentration of the solution, and has been determined for some forty-five substances, and from these the relative atomic coefficients of the constituent elements have been deduced. Similar determinations have also been made with some metals and with organic compounds. For example, from the cases of water, sodium chloride, and sodium chlorate, the values, for hydrogen 0·05, for oxygen 0·9, are found, the value for water being unity. The value so found for cobalt, 53·9, is intermediate between those for iron and nickel, 45·5 and 59·4 respectively, in good agreement with existing knowledge as to the position of this element in the

periodic table. There is some slight indication that the value for carbon in aromatic compounds is lower than in the aliphatic compounds, and also that that for ferrous iron is lower than for ferric iron, but more exact measurements are required to establish these points.

Plotting the relative atomic absorption-coefficients against the atomic numbers gives an interesting curve with several abrupt changes of slope, the absorption-coefficient increasing continuously with the atomic number, slowly from hydrogen to chromium, then much more rapidly, and, on the average, fairly linearly from chromium to silver, where the slope much decreases. In the region from platinum to bismuth the slope is very steep, whereas for uranium the coefficient is almost twice that of bismuth, the next lower element examined.

The values of the relative atomic absorption-coefficients of the elements determined are set forth in the following table:

Atomic number	1	6	7	8	11	12	13	14	15
Element ...	H	C	N	O	Na	Mg	Al	Si	P
Rel. at. abs. coeff.	0·05	0·46	0·63	0·9	1·9	3·5	3·4	4·1	5·68
Atomic number	16	17	19	20	24	25	26	27	28
Element ...	S	Cl	K	Ca	Cr	Mn	Fe	Co	Ni
Rel. at. abs. coeff.	7·78	9·5	11·1	14·4	24·1	41·4	45·5	53·9	59·4
Atomic number	29	30	33	35	38	42	47	48	50
Element ...	Cu	Zn	As	Br	Sr	Mo	Ag	Cd	Sn
Rel. at. abs. coeff.	65·1	75·4	128	154	173	244	300	301	311
Atomic number	52	56	58	74	78	80	82	83	92
Element ...	I	Ba	Ce	W	Pt	Hg	Pb	Bi	U
Rel. at. abs. coeff.	315	334	327	308	529	547	569	677	1123

The *X*-rays used were from a bulb with tungsten anticathode, filtered through an aluminium screen 1·25 mm. thick. For the reasons referred to at the commencement, the rays, though not homogeneous, probably behaved in the same way as homogeneous *X*-rays, although the value for tungsten is doubtless vitiated by selective absorption. An increase in absorption occurs apparently with solutions in the colloidal state. F. S.

Initial Charged Condition of the Active Deposits of Radium, Thorium, and Actinium. G. H. HENDERSON (*Trans. Roy. Soc. Canada*, 1917, [iii], **10**, 151—167).—The requirements of the testing vessel to enable the percentage to be determined of the atoms recoiling from the emanations which are neutral or charged are discussed, and an apparatus for this purpose described. In dry air all the residual atoms are probably positively charged, whereas in pure ether vapour, and probably in pure water

vapour, all of them are uncharged. In a mixture of air and vapour, the proportion of neutral and positively charged atoms depends on the proportion of the mixture. This seems to be general, hydrogen, oxygen, carbon dioxide, etc., giving all positive, ether, water, and ethyl bromide vapours giving all neutral recoiling atoms. Though differences exist in the behaviour of the three emanations, it is probable that all three types of recoiling atom are similarly affected by the surrounding gas and the electric field. The charged or neutral condition of the recoiling atom is not a consequence of what occurs at the disintegration, but must be ascribed to the gas molecules encountered during its recoil. Collision with certain gas molecules ionises it as well as the molecule struck, whereas with others, whatever its state before collision, after collision it escapes always uncharged. The character of the charge carried at the instant of its formation from the emanation atom does not affect the problem, and is not discussed. F. S.

The Motion of Ions and Electrons through Gases. E. M. WELLISCH (*Phil. Mag.*, 1917, [vi], **34**, 33—66).—In previous experiments on the mobility of ions in air at varying pressures, it has been found that the increase in the value of the product of the mobility and the pressure for negative ions at low pressures is due to the fact that electrons and ions act as carriers, and that the proportion of the current carried by the electrons increases as the pressure is reduced. When the ions alone are considered, the product of mobility and gas pressure remains constant. Further experiments on the mobility of the negative ions in hydrogen and carbon dioxide have given the same result in that the mobility of the negative ions varies inversely as the pressure of the gas.

The proportion of electrons to ions in a gas at a given pressure is known to depend very largely on the nature of the gas, and it appears that gases and vapours which contain electronegative elements are favourable to the formation of negative ions. The vapour of light petroleum contains a very small proportion of negative ions, but a trace of an active substance is sufficient to produce a large number of ionic carriers, a result which agrees with previous experiments on inert gases.

The investigation of the motion of the electrons through carbon dioxide has given results which suggest that the electron may traverse a considerable distance with accelerated motion before its final velocity is acquired. There was no evidence of any change in the nature of either the positive or the negative ion when the pressure of the gases experimented on was reduced.

The results are discussed in reference to various problems connected with the ionisation of gases. H. M. D.

The Discharge Potentials of Ions on Heated Electrodes. I. JNANENDRA CHANDRA GHOSH (*J. Physical Chem.*, 1917, **21**, 426—432).—Measurements of the discharge potential were made for the chlorine, bromine, sulphate, and nitrate ions at 30° and

96°. The temperature of the platinum wire anode was varied by passing a suitable current through a circuit, of which the anode formed part. The results obtained indicate that the phenomenon of overvoltage has disappeared at the higher temperature, and further, that the discharge potentials for the chlorine and bromine ions at 96° are less than their respective normal electrode potentials. H. M. D.

Photoelectric Ionisation of Solutions. MAX VOLMER (*Zeitsch. wiss. Photochem.*, 1917, **16**, 186—189).—Under the influence of ultra-violet rays of very short wave-length, solutions of anthracene in hexane show a very large increase in their electrical conductivity. In the apparatus used by the author for the investigation of this effect, the conducting power of the illuminated solution was one to two thousand times as great as that of the same solution in the dark. The same effect has been found with solutions of methylanthracene, phenanthrene, chrysene, stilbene, α- and β-naphthol, diphenylamine, α-naphthylamine, quinizarine, and naphthazarine. In all cases the active rays are of wave-length less than $\lambda = 225\ \mu\mu$. H. M. D.

Measurement of Oxidation Potentials at Mercury Electrodes. II. The Chromic–Chromous Potential. GEORGE SHANNON FORBES and HERMAN WILLIAM RICHTER (*J. Amer. Chem. Soc.*, 1917, **39**, 1140—1148. Compare A., 1914, ii, 795).—Using the same method as previously adopted for measurement of the stannic–stannous potential (*loc. cit.*), the authors have determined the oxidation potential of chromic–chromous chloride. Pure violet chromic chloride was partly reduced to chromous chloride by heating in a current of hydrogen in a quartz tube at 400°. The mixture was dissolved in ice-cold $0\cdot1N$-hydrochloric acid. The solution thus prepared was filtered into the cell and allowed to remain over pure mercury. When all operations were carried out in either hydrogen or carbon dioxide absolutely free from oxygen, the potential rose continuously to a maximum constant value, which was reached in two days. If oxygen was present even in traces, the potential fluctuated irregularly. When the equilibrium potential had been obtained, the solution was analysed. Referred to the normal hydrogen electrode as zero, with correction for junction potentials, and at 25° $\pi = -0\cdot400 + 0\cdot065 \log Cr^{III}/Cr^{II}$. On platinum, the potentials reached a maximum about 0·16 volt lower than that on mercury, with the evolution of hydrogen. J. F. S.

Applicability of the Isohydric Principle to Decinormal Mixtures of Hydrochloric Acid and Potassium Chloride. N. EDWARD LOOMIS, J. L. ESSEX, and MERLE R. MEACHAM (*J. Amer. Chem. Soc.*, 1917, **39**, 1133—1139. Compare this vol., ii, 13).—It was previously shown (*loc. cit.*) that the potential of a $0\cdot1N$-potassium chloride calomel electrode is identical with that of a $0\cdot1N$-hydrochloric acid calomel electrode. This indicates that at the concentration $0\cdot1N$ these two substances are equally dissociated. In

accordance with the isohydric principle it follows that if $0{\cdot}1N$-potassium chloride and hydrochloric acid are equally dissociated, these solutions may be mixed in any proportion without changing their degree of dissociation, and in such a mixture, both substances will have that degree of dissociation which they would have had had they been present alone in the same volume. With the object of testing this, the *E.M.F.* of cells of the type H_2,Pt|$0{\cdot}1N$(HCl+KCl)|Hg_2Cl_2|Hg have been measured, in which the sum of the hydrochloric acid and potassium chloride is $0{\cdot}1N$ and in which the hydrochloric acid varies between $0{\cdot}01N$ and $0{\cdot}09N$ and the potassium chloride varies between $0{\cdot}09N$ and $0{\cdot}01N$. In every case it is shown that the *E.M.F.* of the system is higher than the value calculated from the isohydric principle. This result has been explained by the conclusion that the isohydric principle does not apply rigidly, but that there is a slight increase in the dissociation of the hydrochloric acid with increasing proportions of potassium chloride. In the most extreme case, the mixture of $0{\cdot}01N$-HCl+$0{\cdot}09N$-KCl, the dissociation of the acid appears to have increased from 86% to 86·68%. The reason for this increase is not definitely indicated by the present work. J. F. S.

Inclusions in Silver Voltameter Deposits and the Electrochemical Equivalent of Silver. W. M. Bovard and G. A. Hulett (*J. Amer. Chem. Soc.*, 1917, **39**, 1077—1103. Compare A., 1916, ii, 213).—In a previous paper (*loc. cit.*) the nature and amount of the inclusions in the cathode deposit of various silver voltameters were determined. The present paper deals with an experimental comparison of the anode loss and cathode gain in silver voltameters. A special form of voltameter, based on that devised by Smith (*Nat. Phys. Lab.*, 1910, 32) has been used, and it is shown that the loss from a silver anode agrees with the cathode gain to within 7 parts per 100,000 when the weight of the cathode deposit is corrected for inclusions. This error is to be regarded as a maximum, since the process involves considerable manipulation, which would tend to make the divergence between the two quantities larger. An improved apparatus is described for measuring the amount of inclusions, and this gives an accuracy of 0·001%. The amount of inclusions in the deposit on a standard platinum cup voltameter has been found to be 6·7 parts per 100,000. Calculating from this value, it is shown that the value of the electrochemical equivalent of silver is 1·11798 and the value of the faraday is 96,496. The inclusions in deposits on silver cathodes are of the same value as those on platinum to within 1 part per 100,000, a value of 7·7 per 100,000 having been obtained. The silver deposit on a silver wire in the special form of apparatus used for the anode loss and cathode gain comparison has been found to contain very large amounts of inclusions. The explanation of this has not been discovered. The values obtained for the faraday by means of (*a*) the silver voltameter, (*b*) the iodine voltameter, and (*c*) the cadmium voltameter have been compared. The divergence is attributed to a possible error in the atomic weight of cadmium. J. F. S.

The Hydration of Ions and Metal Overvoltage. EDGAR NEWBERY (T., 1917, **111**, 470—489. Compare this vol., ii, 64).—The cathodic and anodic overvoltages of a number of metals have been investigated in sulphate, nitrate, and chloride solutions, attention being directed to the influence of time and of current density on the overvoltage. Some observations were also made on solutions containing colloidal substances.

In general, the cathodic overvoltages are less than 0·05 volt, but are much higher for iron, nickel, and cobalt. The anodic overvoltages are also low unless the metal deposition is accompanied by passivity. This was observed with iron, nickel, and thallium. The results obtained support the view that metal overvoltages are mainly due to the formation of solid solutions of hydrides, higher oxides, etc., on or in the electrodes. The cathodic solid solutions are very dilute except in the case of iron, nickel, and cobalt, and it is to this circumstance that the high overvoltages shown by these three metals are to be attributed. The presence of hydrides in these three metals has affected all previous determinations of the normal potentials of these metals, and a reinvestigation of these potential differences has shown that accurate and reproducible values can only be obtained in the absence of free hydrogen and metallic hydrides. Even in these circumstances the value of the single potential difference for the three metals in question is not quite determinate, for rapid motion of the electrode relative to the electrolyte produces an appreciable change. This phenomenon is supposed to be connected with the hydration of the corresponding ions, which are thus similar to the hydrogen and hydroxyl ions, whilst most other ions appear to be non-hydrated.

The hydrated and non-hydrated ions behave differently towards colloids, in that these are carried into the metal surface by hydrated ions only and have no influence on overvoltage and little or none on the nature of the deposited metal unless hydrated ions are involved in the electrolytic process.

Previous attempts to determine ionic hydration by the use of a reference substance are criticised adversely. H. M. D.

Electroreduction of the Nitrates of Potassium and Lithium by the Alternating Current. J. KLIATCHKO and CH. BINGGELY (*Ann. chim. anal.*, 1917, **22**, 81—84).—Various metals were used as electrodes, either fixed or rotating. Both with lithium and potassium nitrate the best reduction was obtained with electrodes of cadmium, the least reduction being obtained with copper. There was always a greater reduction with rotating than with fixed electrodes, and in all cases the electrodes became coated with a more or less thick layer of oxide, this being particularly marked for aluminium. The more dilute the solution of the electrolyte, the higher was the percentage reduction. The reduction was increased by the presence of sulphuric acid, but in these cases there was a rapid destruction of the electrode. W. G.

Magneto-chemistry of the Compounds of Chromium. I. Chromic Sulphate and Nitrate. B. CABRERA and M. MARQUINA (*Anal. Fis. Quim.*, 1917, **15**, 199—209).—An account of the deter-

mination of the magneto-chemical data of chromic nitrate, and of the violet and green chromic sulphates. A. J. W.

Dilatability of Argon and Neon. Internal Pressure in Monatomic Gases. A. LEDUC (*Compt. rend.*, 1917, **164**, 1003—1005).—The coefficients of dilatability of argon and neon were found experimentally to be $3669 . 10^{-6}$ and $3664 . 10^{-6}$ respectively, from which, by calculation, their internal pressures are determined as $190 . 10^{-5}$ atmos. and $53 . 10^{-5}$ atmos., which values support the hypothesis that the internal pressures in monatomic gases are proportional to the squares of their molecular masses. W. G.

Changes in the Expansion of Alloys of Iron and Nickel under the Action of Different Thermal or Mechanical Treatments. CH. ÉD. GUILLAUME (*Compt. rend.*, 1917, **164**, 904—906. Compare *ibid.*, 1916, **163**, 654, 741, 966).—The alloys examined had a nickel content varying from 27·5—69·0% of nickel. The alloys were tempered, annealed in the ordinary manner or very slowly in sand, or tempered and drawn. In certain cases, after the slow annealing, the specimens were heated to a red heat and cooled in the air. With the alloys of low nickel content, all the methods of thermal and mechanical treatment resulted in an increase of the coefficient of expansion. For an intermediate nickel content, all the treatments caused a lowering of this coefficient, which was partly permanent after reheating and cooling in air. The alloys with higher nickel content, 42—69%, behaved in the same manner as invar (*loc. cit.*), but with smaller changes. W. G.

Molecular Attraction. XIV. Specific Heats of the Elements and some Energy Changes. J. E. MILLS (*J. Physical Chem.*, 1917, **21**, 345—381).—The literature of the specific heats of the elements has been examined and the available data utilised in drawing up a series of tables in which the specific heats of the elements are given at various temperatures covering the range over which measurements have been made. In some cases the data for the three states of aggregation are recorded, and these are supplemented by heats of fusion and heats of vaporisation. H. M. D.

Measurement of Cryoscopic Constants at Elevated Temperatures. J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1917, **39**, 1125—1133).—An apparatus is described for the determination of cryoscopic constants at elevated temperatures. It consists of a freezing tube 20 cm. long and 4 cm. diameter; this is placed inside a slightly larger tube which serves as an air-jacket. The two tubes are placed inside the heating chamber, which consists of a long-necked bulb fitted with a wide side-tube at the top and a narrow side-tube at the bottom which makes connexion between the bulb and the top side-tube. A water condenser is attached to the top side-tube and to a manostat. An

automatic stirrer and thermometer are placed in the freezing tube. To obtain the required temperature of the heating jacket, a liquid, preferably a hydrocarbon or mixture of hydrocarbons, is used, and the boiling point is regulated by varying the pressure. Sometimes it is found that the solvent sublimes and condenses in the neck of the tube, thus altering the composition of the solution; this is obviated in the present apparatus by means of an electrically heated platinum spiral. It is shown that this apparatus can be used for a large number of substances covering a wide range of melting points, since it is possible to secure the necessary adiabatic conditions by simply choosing a liquid of an appropriate boiling point for the mantling vapour. It is claimed that the more serious sources of error usually found in such cryoscopic measurements, in particular the errors due to imperfect adiabatic conditions and to the sublimation of the solvent, are removed. The limit of accuracy seems to be limited to the accuracy with which temperatures can be read by the thermometer, namely, 0·001° in the case of a mercury thermometer. To test the apparatus, the cryoscopic constant (K) and the latent heat of fusion (L) of several substances have been determined. The following values are given in the paper: anthracene, $K=68{\cdot}99$, $L=35{\cdot}70$ cal.; acetanilide, $K=69{\cdot}32$, $L=42{\cdot}87$ cal.; benzoic acid, $K=87{\cdot}88$, $L=34{\cdot}80$ cal. In the case of solutions of anthracene in cinnamic acid, the value of K decreases with increasing concentration, from which it is concluded that anthracene associates in cinnamic acid.

J. F. S.

The Nature of Chemical Affinity in the Combustion of Organic Compounds. W. M. Thornton (*Phil. Mag.*, 1917, [vi], **34**, 66—70).—By reference to the data for the aliphatic hydrocarbons, it is shown that the heat of combustion, H, is related to the molecular weight (m_1) of the hydrocarbon, and the weight (m_2) of the oxygen atoms required for its complete combustion by the equation $H^2/m_1m_2=\text{constant}$. As a matter of fact, the value of this expression falls slightly at first as the molecular weight of the hydrocarbon increases, but soon becomes constant.

This constancy is supposed to afford evidence in favour of the view that the operation of chemical affinity is governed by a law of the gravitational type. In support of this view, the author quotes the results of Bone's experiments on the distribution of oxygen between methane and hydrogen. These experiments showed that in a mixture of the composition $CH_4+O_2+H_2$ at high initial pressure, 97·1% of the oxygen reacted with methane and only 2·9% with hydrogen. The products of the masses corresponding with complete combustion are respectively 16×64 and 2×16, giving a ratio 32 : 1, which is very close to the experimentally observed ratio of distribution in the explosion experiments.

H. M. D.

The Volumes of the Atoms at Absolute Zero. Gervaise Le Bas (*Chem. News*, 1917, **116**, 1—2).—An attempt is made to

estimate the volumes occupied by different atoms in a state of chemical combination at absolute zero. The atomic volume of combined hydrogen is 2·340, and the relative volumes of other atoms are given by the equations C=4H, N=4H, Cl=6H, O_2=5H, >O=3H.

The ratio of the critical volume to the volume at absolute zero is 4·11, and from the data for the aliphatic hydrocarbons the author draws the conclusion that the molecular volume at absolute zero (V_0) is connected with the molecular refractivity (M_a) by the equation $V_0/M_a=3·0$. H. M. D.

Molecular Constitution of Pure Liquids. III. P. N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1728—1744. Compare this vol., ii, 293).—Examination of the values of N for nineteen liquid compounds of different chemical characters over a widely reduced temperature interval shows that in most cases this magnitude varies with the temperature. Practical constancy is observed with methyl formate and stannic chloride, and the remaining compounds are divided into three groups: (1) With methyl, ethyl, and propyl alcohols, acetic acid and water, the value of N at first decreases to a minimum as the temperature rises, and afterwards gradually increases to the temperature of crystallisation; an indistinct minimum also occurs with *n*-hexane, *n*-heptane, *n*-octane, and di*iso*butyl. (2) With benzene, chloro-, bromo-, iodo-, or fluoro-benzene, *n*-pentane, di*iso*propyl, *cyclo*hexane, and methyl formate, small variations in the value of N are observed, but these are so small and irregular that independency of the temperature may be assumed; in the neighbourhood of the critical temperature N increases.

With the saturated hydrocarbons at identical reduced temperatures, the ratio of the abnormality number N to the total number of atoms in the molecule is independent of the molecular weight of the hydrocarbon, so that $N_{\text{corr.}}:n$ is a universal constant; the ratio $N:n$ is termed the atomic coefficient of abnormality. This ratio varies only slightly with the temperature. Structural isomerism has but little influence on the molecular constitution of liquids as expressed by the abnormality number.

The numerical magnitude of the influence of ring-closure on the value of N in the case of *cyclo*hexane is $-0·06766$; thus, the closure of the ring increases the association or diminishes the dissociation of a liquid, whereas introduction of a new carbon or hydrogen atom into the molecule decreases the association or increases the dissociation. The coefficient of abnormality of the double linking, calculated from the value for ethylene, is $+0·06525$, such linking diminishing the association or increasing the dissociation. The above values refer in all cases to the reduced temperature 0·9829.

If the benzene molecule is regarded as a closed ring, its abnormality number is in agreement with the presence of three (actually 2·98) double linkings in the molecule.

The atomic abnormality-coefficient for carbonyl oxygen is 0·15068 with acetaldehyde and 0·14199 with acetone, the mean being 0·14634. For hydroxylic oxygen, however, the atomic coefficient of abnormality, even for one and the same reduced temperature, is not a constant magnitude, but diminishes as the number of atoms in the molecule increases. At the reduced temperature 0·6054, the value of this coefficient is 7·774, 6·152, and 3·950 for the oxygen in methyl, ethyl, and propyl alcohols respectively. The value for the chlorine atom is virtually constant, being 0·2416, 0·2316, 0·2229, 0·2307, 0·2337, and 0·2292 for methyl, ethyl, and propyl chlorides, chloroform, carbon tetrachloride, and chlorine itself at the reduced temperature 0·6054. For the nitrogen atom at the same reduced temperature the value is 0·1696, 0·18478, 0·17810, 0·15820, 0·28083, 0·27718, and 0·26979 with nitrogen itself, ammonia, ethylamine, propylamine, aceto-, propio-, and butyro-nitriles respectively.

The abnormality number of a liquid is a constant number and is unchanged by chemical reaction, so that in chemical changes between liquids the number of the reacting molecules is equal to the number of the resultant molecules if corresponding temperatures are employed in all cases. Further, if the molar volumes of the four liquids taking part in the reaction, $A_1+A_2=A_3+A_4$, are v_1, v_2, v_3, and v_4 respectively, and their abnormality numbers at corresponding temperatures N_1, N_2, N_3, and N_4, it is readily shown that $N_1+N_2=N_3+N_4$ if $v_1+v_2=v_3+v_4$, that is, the molar volumes of the liquid compounds taking part in a chemical reaction are not changed in magnitude if the initial system consists of the same number of molecules as the final system. T. H. P.

Measurement of the Absolute Viscosity of very Viscous Media. S. E. SHEPPARD (*J. Ind. Eng. Chem.*, 1917, **9**, 523—527).—The application of Stokes's law connecting the rate of fall of a spherical substance with the viscosity of the medium is discussed in reference to very viscous media, and particularly with regard to the influence of the boundary walls of the containing cylinder. Stokes's law assumes the medium to be infinite in extent compared with the diameter of the sphere, that is, T is constant when $R'/R=r=\infty$, where T is the time of fall through length S and R' and R are the respective radii of the cylinder and the sphere. An empirical formula is worked out which corrects for the influence of the boundary wall and is valid over a wide range, namely, $T=T_\infty+C/(r-1)^n$, where T_∞ is the constant value of T where $r=\infty$ and C and n are constants. Using this formula and a linear correction for the total height of the liquid column, absolute determinations of viscosity of very viscous media may be made with quite simple apparatus by the application of Stokes's law, the complete equation being $K=2R^2/9S(s-s')g\,.\,[T-C/(r-1)^2]$, n being taken as 2 and C depending on the diameter of the sphere, whilst s, s' are the densities of the sphere and the medium, and g the acceleration of gravity. G. F. M.

Viscosity of Binary Systems containing Stannic or Antimony Chloride. N. S. KURNAKOV, S. I. PERLMUTTER, and F. P. KANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1658—1693. Compare A., 1913, ii, 190, 388; 1915, ii, 232, 423, 524).—The authors have investigated the viscosities of the binary systems formed by antimony trichloride with ethyl ether or acetone and those formed by stannic chloride with ethyl formate, acetate, or butyrate, propyl formate, ethyl benzoate, or benzene. With the exception of the system stannic chloride–benzene, each of these systems exhibits external signs of chemical action—heating of the liquid or deposition of the solid compound. The formation of the latter necessitates the choice of a suitable temperature for measuring the viscosity isotherms in the liquid condition.

With the system antimony trichloride–ethyl ether, the viscosity isotherms become increasingly flat as the temperature is raised and the maxima are displaced more and more towards the more viscous component, namely, antimony trichloride. At low temperatures the maximal viscosity corresponds approximately with the ratio $SbCl_3:Et_2O=4:1$, but, in consequence of the dissociation of the compound in the liquid state, the solid phase may be assumed to have the composition $(SbCl_3)_n,Et_2O$, where $n=2$ or 3.

For acetone the value 0·00339 is found for η_{25}; calculation from Thorpe and Rodger's results (T., 1894, 782) gives the value 0·00317, whereas Jones and Mahin (A., 1909, ii, 539, 957) found 0·00346. The general course of the viscosity curves for mixtures of acetone and antimony trichloride is similar to that observed with the preceding system. The isotherms for 50° and 80° exhibit an irrational, flat maximum for 77—80 mols. % $SbCl_3$, the position of this moving in the direction of the antimony chloride as the temperature is raised. Here, too, the existence in the liquid state of a dissociated compound, $(SbCl_3)_n,COMe_2$, where $n=2$ or 3, may be assumed.

In spite of the pronounced development of heat, sometimes as high as 5800 cals. per gram-molecule, occurring when stannic chloride is mixed with an ester of a monobasic acid, the mixtures remain liquid over considerable ranges of temperature and yield characteristic viscosity diagrams. For esters of one and the same alkyl radicle, the heat effect in these systems gradually falls as the molecular weight of the organic acid increases, the maximum viscosity undergoing a corresponding diminution. Replacement of the ethyl radicle of ethyl formate by propyl or methyl produces little change in the magnitude of the viscosity of the system. The viscosity isotherms at 25—75° and their temperature-coefficients are continuous curves with sharply marked maxima at about 33·3—40 mols. % of stannic chloride. For the system containing ethyl formate or acetate, the maxima of the viscosity diagrams correspond with 1 mol. of stannic chloride to 2 mols. of the ester. With ethyl butyrate or benzoate, however, the maxima of the isotherms are flatter and undergo displacement towards the stannic chloride as the temperature is raised from 25° to 75°, owing to increasing dissociation of the compound, $SnCl_4,2R\cdot CO_2Et$. The

existence of these compounds is confirmed by investigating the composition of the solid phase separating on cooling the liquid solution, either by chemical analysis or by determining the distectic point in the corresponding fusion diagram. In the case of the system stannic chloride–ethyl benzoate, the fusion diagram shows, besides the distectic, $SnCl_4,2Ph\cdot CO_2Et$, also a maximum melting point corresponding with another solid compound, $SnCl_4,Ph\cdot CO_2Et$ (compare Pfeiffer, A., 1914, i, 923; ii, 568).

When stannic chloride and benzene are mixed, marked cooling takes place. The viscosity isotherms for 25° and 70° are widely different from those of the above systems and consist of almost straight lines with a slight convexity towards the axis of concentration. These results are in accord with those of Schulze and Hock (A., 1914, ii, 186) referring to the vapour pressures of the same system.

From the above results the authors conclude that the active factor determining the process of chemical interaction in these systems is the presence of oxygen in the compound with which the stannic or antimony chloride is mixed. T. H. P.

Viscosity of the System Stannic Chloride–Ethyl Propionate. N. S. KURNAKOV and N. N. BEKETOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1694—1701).—The existence of a singular or Dalton point in the viscosity–composition curve of a system is a necessary condition for the detection of a definite chemical compound. When the curve is continuous, the composition corresponding with the maximal point does not usually remain constant when the equilibrium factors of the system undergo change, and is not expressed by rational atomic or molecular proportions. For the system stannic chloride–ethyl propionate, the viscosity isotherms for 25° and 70° represent continuous curves with characteristic maxima at about 35 mols. % of stannic chloride. The position of the maxima is intermediate to those observed with the systems formed by stannic chloride with ethyl acetate and butyrate respectively, and the values of the maxima at 25° for the systems of this series are: ethyl formate, less than 0·6; acetate, 0·50318; propionate, 0·21400; and butyrate, 0·19828. The close approximation of the position of the maxima to the molecular ratio,

$$SnCl_4 : C_2H_5\cdot CO_2Et = 1 : 2,$$

indicates that the compound, $SnCl_4,2C_2H_5\cdot CO_2Et$, is only slightly dissociated in the liquid. This compound does indeed separate in crystals, m. p. 45·2°.

The curves connecting D_4^{25} and D_4^{70} with the composition have also been traced for this system, and are found to change in direction at points corresponding closely with the maximal viscosities.

T. H. P.

The Internal Friction of Aqueous Salt Solutions. W. HERZ (*Zeitsch. anorg. Chem.*, 1917, **99**, 132—136. Compare A., 1914, ii, 338; 1915, ii, 423).—Curves are given to show that, for a number of salts of univalent and bivalent metals, the absolute

fluidity is directly proportional to the specific volume of the solution. In the case of potassium and ammonium halogen salts, this is only true of higher concentrations, dilute solutions exhibiting a minimum fluidity. C. H. D.

The Adsorption of Sulphur Dioxide by Charcoal at $-10°$. A. M. WILLIAMS (*Proc. Roy. Soc. Edin.*, 1916, **37**, 161—172).—The relation between the pressure and the quantity of sulphur dioxide adsorbed by blood charcoal at $-10°$ has been examined. The adsorption isotherm is of the normal type, and follows the same course as that previously found for the adsorption of water vapour.

Calorimetric observations show how the heat of adsorption at constant volume varies with the degree of adsorption. The curve expressing the relation between these quantities is of complex type and shows a minimum and a maximum, for which an explanation is offered. H. M. D.

Liquid Films in Capillary Tubes. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 407—425).—Extracts from previous papers on capillary phenomena and the wetting of solids by liquids are given, and these are considered to warrant the conclusion that the rise of a liquid in a capillary tube is independent of the nature of the material of the tube provided this is wetted by the liquid. The experiments made by Bigelow and Hunter (A., 1911, ii, 471), which led these authors to the opposite conclusion, are criticised on the ground that the method which these investigators employed does not afford a measure of the adhesion of the liquid to the wall of the tube, since the liquid is not removed from the wall. It is considered that the results in question depend on the conditions which determine the displacement of a liquid from a wetted surface by air. H. M. D.

Technique of Preparing Membranes for Dialysis. WILLIAM BROWN (*Biochem. J.*, 1917, **11**, 40—57. Compare A., 1915, ii, 824).—The author describes the preparation of membranes of graded permeability made of collodion for use in water, chloroform, benzene, etc.; of agar and gelatin in alcohol, acetone, benzene, etc.; of formalised gelatin in water, etc. The general principle underlying the preparation of these membranes is that if a system consisting of liquid *A*–membrane substance–liquid *B* be such that (1) the membrane substance only imbibes a negligible amount of *A*, (2) the membrane substance strongly imbibes *B*, and (3) *A* and *B* are miscible in all proportions, then membranes of graded permeability for use in liquid *A* can be prepared by immersing films of the membrane substance in mixtures of *A* and *B* and transferring to liquid *A*. Graded membranes for use in liquid *B* can be prepared only when a method exists of suppressing the capacity of the membrane substance to imbibe *B*, this suppression being brought about at the stage where the membranes are still immersed in the mixture of *A* and *B*. The graded membranes of formalised gelatin are prepared in accordance with the latter method. They are found to be

very useful in the purification of certain enzymes and in the investigation of phenomena of selective permeability. H. W. B.

The Selective Properties of the Copper Ferrocyanide Membrane. FRANK TINKER (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 268—276).—Measurements have been made of the changes which take place in the concentration of sucrose solutions subjected to the action of colloidal copper ferrocyanide. In consequence of selective absorption of the water, the concentration of the solutions increases. The quantity of water absorbed at the ordinary temperature decreases as the strength of the sucrose solution increases, and for 100 grams of the dry ferrocyanide was found to diminish from about 30 grams for pure water to 13—14 grams for a 60% solution of sucrose. The curves showing the relation between the quantity of absorbed water and the concentration of the solution tend to become parallel to the concentration axis, and this is said to indicate the formation of a hydrate of the composition $Cu_2FeCy_6,3H_2O$, which corresponds with 15·7 parts of water per 100 of ferrocyanide. The excess quantity of water taken up from more dilute solutions is said to be adsorbed. In favour of this view, it is pointed out that there is no simple relation between the excess and the concentration of the sucrose solution, nor is the amount taken up from a given solution constant when different samples of the ferrocyanide are made use of. This variation is attributed to variations in the surface area of different samples.

The evidence afforded by these experiments is in favour of the theory that the selective permeability of colloidal membranes is the result of preferential adsorption. H. M. D.

Drainage of Crystals. NORRIS FOLGER HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1148—1152).—A mathematical paper in which the efficacy of centrifugal drainage of crystals in fractional crystallisation is considered. It is shown that the common practice of using only gravitational drainage in the case of the rare earth and similar separations is well founded, since the extra time and trouble required for centrifugal drainage would more than outweigh the relatively small gain in efficiency. On the other hand, in the separation of very dissimilar substances, especially those with flat solubility curves, the attendant great increase in the speed of purification justifies almost any amount of pains taken in washing and drainage. J. F. S.

Velocity of Crystallisation in Under-cooled Fusions. R. NACKEN (*Centr. Min.*, 1917, 191—203. Compare A., 1916, ii, 130).—Further experiments were made with salol (m. p. 41·75°). The material was crystallised between slips of glass maintained at a definite temperature by a stream of water, and observed under the microscope. The rates of growth are given for different crystal faces and edges; in each case the rate increases with the fall in temperature below the melting point. L. J. S.

The Nucleus Method for the Preparation of Colloidal Metallic Solutions of Definite Properties. RICHARD ZSIGMONDY (*Zeitsch. anorg. Chem.*, 1917, **99**, 105—117).—Colloidal solutions in which all the particles are of equal size are obtained in the case of gold ruby glass, and occasionally when the formaldehyde method is employed in the preparation of colloidal gold. Very uniform solutions are obtained by adding solutions containing nuclei, prepared by the reduction of slightly alkaline solutions of gold with phosphorus (A., 1906, ii, 679). These nuclei grow by deposition, and the number of particles is determined by the quantity of the nuclear solution added. The spontaneous formation of nuclei may be suppressed without hindering growth by the addition of ammonia or of potassium ferrocyanide or ferricyanide, whilst growth may be diminished without appreciably altering the formation of nuclei by the addition of alkali haloids, hydrogen sulphide, or colloidal sulphur.

[With C. HIEGE.]—When the spontaneous formation of nuclei is suppressed by the addition of a reagent, the number of submicrons is found to be strictly proportional to the volume of the nuclear solution added, the diameter of the particles in the latter being 3·5 $\mu\mu$. Reduction with hydrogen peroxide in slightly acid solution also gives rise to very little spontaneous formation of nuclei.

[With J. REITSTÖTTER.]—A second method is to use a solution in which growth is so rapid that the supply of gold is exhausted before the spontaneous formation of nuclei has become appreciable. Using water which has been distilled from permanganate with a gold condenser, and adding the nuclear solution to the gold chloride before adding hydroxylamine hydrochloride, with or without alkali carbonate, very clear, deep red solutions are obtained in which the number of particles is strictly proportional to the volume of nuclear solution. Blue solutions are obtained by using a larger quantity of alkali. Similar results are obtained with hydrazine, the addition of alkali being unnecessary.

Solutions of silver or mercury salts with a reducing agent, which are themselves stable, are rapidly reduced, yielding colloidal solutions when a solution containing gold nuclei is added.

C. H. D.

Effect of Freezing on certain Inorganic Hydrogels. H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1917, **39**, 1103—1125. Compare A., 1916, ii, 230).—In a previous paper it was shown that the water in moist hydrogels is present in three forms, free water, capillary water, and combined water. In the present paper the authors describe dilatometric experiments whereby the amount of combined water present has been determined. Experiments were made with the hydrogels of alumina, ferric oxide, and silica. In the case of alumina, the amount of combined water is 37·83%, whereas $Al(OH)_3$ only requires 34·6%; the excess of water is regarded as being present as a solid solution. In the case of ferric oxide, the amount of combined water present

appears to depend on the method of preparation and previous treatment of the hydrogel. The results indicate that combined water is slowly given off on heating the hydrogel with water, and that there is no tendency to form compounds in which the ratio $Fe_2O_3:H_2O$ is simple. The evidence all points to the combination between ferric oxide and water being in indefinite proportions, that is, a solid solution is formed. Silicic acid hydrogels which have not been heated give fairly constant results, the combined water amounting to somewhat above 30%. On digesting with water, the amount of combined water gradually decreases until, after seven days, it reaches one mol. The evidence suggests that a part of the water in all three hydrogels is combined in indefinite proportions. A discussion is entered into as to the nature of the combined water. A few determinations of capillary water are included in the paper; in the case of alumina, the capillary water is very small in quantity, and this becomes less after freezing. In the case of ferric oxide, repeated freezing diminishes the amount of capillary water, but long-continued heating brings about the same result to a much more marked extent. In the case of silica, capillary water is not eliminated by freezing. Instead, water appears to be reabsorbed when the ice has melted. The amount of capillary water contained in silica hydrogel is decreased by digesting on a steam-bath. J. F. S.

The Sensitisation for Agglutination of Suspensoid Colloids by Non-electrolytes with Capillary Activity. H. FREUNDLICH and P. RONA (*Biochem. Zeitsch.*, 1917, **81**, 87—106). —Substances of capillary activity, such as amyl alcohol, the urethanes, phenylthiocarbamide, camphor, and thymol, increase the flocculation sensitivity of the iron hydroxide hydrosol by electrolytes, that is to say, they cause a diminution of the concentration of the electrolytes which will cause the precipitation. This increased sensitivity can be only demonstrated when salts with univalent anions (the flocculating power of which is small), such as Cl', Br', I', NO_3', are employed. No sensitisation can be detected with the salt of greater agglutinating capacity, such as those containing F', SO_4', and citrate ions. In the case of the urethanes, the greater the capillary activity the greater the sensitising power. Substances such as camphor and thymol, which have greater capillary activity, diminish the rate of movement of the iron hydroxide sol in an electric field. The explanation of the action of the non-electrolytes is as follows. They are adsorbed on the surface of the sol particles, and in consequence of the fact that their dielectric constants are smaller than that of water, they diminish the charge on the surface. In consequence, the particles are agglutinated by smaller amounts of the ions which carry an opposite charge, and the sol is therefore precipitated by a smaller amount of electrolyte. Attention is directed to the fact that this sensitisation by non-electrolytes may play an important part in biological phenomena, and explain the precipitation of certain substances, such as nucleoproteins, by narcotics. In the latter

case, the salts present are the real precipitants, the narcotics merely acting as sensitisers of the suspensoid colloids. S. B. S.

Coagulation. R. ZSIGMONDY (*Zeitsch. Elektrochem.*, 1917, **23**, 148—154).—Gold sols have been treated with measured quantities of solutions of sodium chloride, strontium chloride, aluminium nitrate, and thorium nitrate of various concentrations, and the time required for coagulation to occur has been measured. In this case, the coagulation is known to have taken place when the red solution has changed to a well-marked and easily recognised violet solution. In every case it is shown that there is a region in the concentration range of the electrolyte of minimum coagulation time. This concentration is already reached at moderate strengths ($0{\cdot}01N$—$0{\cdot}1N$) of most electrolytes. This region stretches over a considerable range of concentration, but by gradually increasing the concentration still further there is a passage into a region of slow coagulation through a somewhat narrow zone in which small changes in the concentration bring about very large changes in the coagulation time. In this region (Schwellenzone) the coagulation time lies at different places according to the time of observation. Two regions can therefore be differentiated in which a change in the concentration of the electrolyte has no effect on the stability or coagulation time of the gold sol: (1) the region below the "swelling zone," and (2) the region of greatest coagulation velocity. Both pass into one another through the region in which the coagulation time is strongly influenced by the concentration of the electrolyte.
J. F. S.

Adsorptive Stratification in Gels. II. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1917, **11**, 14—20. Compare A., 1916, ii, 474).—Experiments are described which support the view that the occurrence of stratification in gels is dependent on the number of crystallisation centres produced, and that this quantity is affected by the properties of the gel in which the reaction takes place. Solutions which produce a banded precipitate in gelatin may not do so in agar or some other medium. The extent of dilution of the reacting substances also is often an important factor in determining stratification in gels. The experiments are discussed in the light afforded by the microscopical observation of the changes occurring during stratification. H. W. B.

The Dieterici Equation of State. F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1229—1235).—A mathematical paper in which it is shown that the Dieterici equation of state is of the correct form, and that it degenerates into the van der Waals's equation for a gas under low pressure. The equation of Dieterici might therefore be expected to have a much wider range of validity than one of the van der Waals's type. A new method of calculating a is described, and the values so obtained are compared with those calculated by other methods. The agreement between the various values in most cases is very good. J. F. S.

Direction of Spontaneous Transformations. N. V. Tancov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1654—1658).—The author discusses the rule advanced by Ostwald (A., 1897, ii, 308), but combated by Wald (A., 1898, ii, 112), according to which, during a transition from a particular state to one of greater stability, the change is not necessarily to the most stable, but to the nearest. The conclusion now drawn from a consideration of the transformations of sulphur is that Ostwald's theory is strictly applicable only on one side of the transformation temperature, namely, below it. It is shown, further, that during spontaneous transformation at constant volume, the first condition reached is that involving the least change of the temperature-coefficient of affinity.

T. H. P.

The Curves of the Periodic Law. W. M. Thornton (*Phil. Mag.*, 1917, [vi], **34**, 70—75).—The periodic curves obtained by plotting the densities or atomic volumes of the elements as a function of the atomic weight are such that smooth curves may be drawn through the maxima or minima of the periodic curves. These smooth curves represent limiting conditions characteristic of atomic configurations, and it is suggested that the actually found periodicity affords evidence that the internal forces holding the atoms pass through a simple periodic change which in its influence on the volume of the atom is complicated by some form of structural hysteresis. H. M. D.

Simple Device for the Automatic and Intermittent Washing of Precipitates. Elbert C. Lathrop (*J. Ind. Eng. Chem.*, 1917, **9**, 527—528).—The apparatus is distinguished from the ordinary constant level device by having a capillary tube through the stopper of the inverted flask in addition to the discharge tube. The hydrostatic pressure required to pull air through the capillary when full of liquid is slightly greater than the height of the capillary rise, and consequently the level of the liquid in the funnel containing the precipitate may sink by this amount below the end of the capillary before air rushes through this into the flask and allows the liquid to discharge until the capillary end is once more covered. The flow is thus intermittent, and by selecting a suitable capillary and a discharge tube of correct length, each addition of solvent drains almost completely from the precipitate before a further quantity is automatically discharged from the container. G. F. M.

Inorganic Chemistry.

Conversion of Hypochlorite into Chlorate in Alkaline Solution. F. FOERSTER and P. DOLCH (*Zeitsch. Elektrochem.*, 1917, **23**, 137—147).—The mechanism of the conversion of alkaline solutions of sodium hypochlorite into sodium chlorate has been

studied. It is shown that at 50° the reaction is of the second order rather than the third, that is, it follows the equation $2NaClO = NaClO_2 + NaCl$ as its first stage. There is also an evolution of oxygen, which evidently occurs according to the equation $2NaClO = O_2 + 2NaCl$. The transformation of chlorite into chlorate is shown to follow the bimolecular reaction $NaClO + NaClO_2 = NaClO_3 + NaCl$. Consequently, the formation of chlorate from hypochlorite occurs according to the equations: (1) $2NaClO = NaClO_2 + NaCl$, and (2) $NaClO + NaClO_2 = NaClO_3 + NaCl$. Of these reactions, the latter occurs much more rapidly than the former. The following velocity constants have been obtained: K_1, 50° = 0·0019, 25° = 0·00010; K_2, 50° = 0·050, 25° = 0·0035. The temperature-coefficient of K_1 is 3·15, whilst that of K_2 is 2·88. The possibility of the formation of chlorite or chlorous acid in the acid decomposition of hypochlorite solutions is discussed. Carlson and Gelhaar (A., 1908, ii, 731) have stated that in the electrolytic production of chlorates, appreciable quantities of chlorites are also formed. The authors have repeated this work, and are unable to find more than the merest trace of chlorite. The fact that the chloride used by Carlson and Gelhaar has been shown to contain bromide furnishes the reason for the presence of chlorites in their experiments. J. F. S.

The Action of Iodine on the Alkalis. J. BOUGAULT (*Compt. rend.*, 1917, **164**, 949—951. Compare Péchard, A., 1899, ii, 593; Zopf, A., 1887, 688, 997).—With sodium hydroxide, iodine probably yields sodium hypoiodite, but this is so rapidly transformed into iodate that in a few minutes the reaction is almost complete. With sodium carbonate, the reactions are identical, but proceed much more slowly. With sodium hydrogen carbonate there is no apparent formation of iodate even after several days, but the presence of hypoiodite can be proved by the slow addition of sodium hyposulphite solution. W. G.

Hydrogen Sulphide Generator. F. K. BEZZENBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1240—1241).—The apparatus described is a modification of the Ostwald generator. It consists of three large bottles, two of which are fitted with side tubulures at the bottom. The larger bottle (*A*) is the acid reservoir and is placed above the others; this is connected by its side-tube, through a valve which only permits downward flow, to the gas reservoir (*B*), and a second tube which also reaches to the bottom of *B* leads to a funnel placed in the neck of *A*. The gas reservoir is connected with the generator (*C*) by a third glass tube, and from *C* the gas is allowed to pass out through a valve similar to the one mentioned above. The main advantage of the apparatus is that the acid, when it is forced out of the generator and gas reservoir, does not pass back to the acid reservoir by the tube by which it enters; this allows the acid to be filtered through glass wool before it reaches the acid reservoir, and so prevents a large accumulation of sulphur. J. F. S.

Reaction of Sulphur Chloride with Metals. Catalytic Action of Ether. N. DOMANICKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1724—1727).—The investigations of Wöhler (*Annalen*, 1850, **73**, 575), Chevreul (*Compt. rend.*, 1867, **64**, 302), Baudrimont (*Compt. rend.*, 1867, **64**, 369), Smith and Oberholtzer (A., 1893, ii, 574), and Nicolardot (A., 1909, ii, 138) have shown that some metals do not react with sulphur chloride either in the cold or on heating, whilst others react only on heating, and in a few cases the reaction begins at the ordinary temperature; the products of the reaction are sulphur and chlorides of the metals, with small proportions of sulphur compounds

The author finds that the reaction may be brought about or greatly accelerated by the agency of dry ether, with which the metallic chlorides form complexes, and so enhance the thermal effect of the reaction. Under these conditions, magnesium, zinc, aluminium, tin, antimony, bismuth, molybdenum, iron, mercury, and gold are readily converted into their chlorides or etherates of the latter. On the other hand, the alkali metals, calcium, cadmium, thallium, lead, tungsten, chromium, manganese, cobalt, nickel, copper, silver, and platinum react either not at all or with extreme slowness. The metals which do react either (1) give chlorides which readily form etherates, as is the case with zinc, aluminium, tin, and bismuth, or (2) give chlorides which are readily fusible and volatile and approximate in their properties to the chloro-anhydrides; in correspondence with the latter, the higher chlorides are mostly formed, for instance, $ZrCl_4$, $FeCl_3$, $HgCl_2$. Univalent metals do not react, and bivalent metals (excepting mercury), if at all, react with far greater difficulty than ter- and quadri-valent metals. It is probable that other metals, giving volatile higher chlorides, such as titanium, germanium, vanadium, and the like, also react readily with sulphur chloride and ether. T. H. P.

The Formation of Diamonds. OTTO RUFF (*Zeitsch. anorg. Chem.*, 1917, **99**, 73—104).—The attempt has been made to repeat systematically the experiments which are stated to have led to the formation of diamonds, and especially to determine whether true equilibrium was reached by introducing small diamonds and measuring any increase. The work being broken off, it has not been possible to repeat the promising experiments of Ludwig (A., 1902, ii, 70, 451), consisting in the fusion of carbon in hydrogen under 1500 atmospheres pressure.

The products are in no cases identified with certainty as diamonds, their size being too small. For detection, the residues are heated with hydrofluoric and nitric acids on the water-bath, then with concentrated sulphuric acid and a crystal of potassium nitrate at 250°, and finally in a stream of chlorine free from oxygen at 950—1000°. Carborundum is destroyed by this process, but diamond is not attacked. Diamonds are detected by their fluorescence in ultra-violet light or α-radiation.

Small diamonds do not increase in weight when heated for

fourteen days in acetylene, coal gas, methane, or carbon monoxide at temperatures up to 790°. On the other hand, a carbon arc in liquid air gives a minute residue of crystals fluorescing like diamonds. A carbon arc through which a spray of water passes continuously gives a minute residue, the fluorescence of which is very faint. Organic vapours mixed with carbon monoxide yield amorphous carbon and graphite, and mixtures of molten organic solids with catalytic agents give entirely negative results. Minute fluorescent diamonds are obtained by Moissan's method of quenching iron or its alloys with titanium, vanadium, tungsten, or molybdenum in water from 1600° or higher. At 2200° the iron on cooling is so full of graphite that there can be no internal pressure. An arc between carbon and an alloy of iron, antimony, and manganese, melting at 850°, is without effect, as is the action of acetylene or coal gas on fusible alloys, or the quenching of fused silicates in a carbon crucible.

Experiments have also been made in an electric furnace under pressures up to 3000 atmospheres, only graphite being formed.

C. H. D.

Carbon Suboxide. Otto Diels (*Ber.*, 1917, **50**, 753—755).—The author points out that the elaborate apparatus recently designed by Stock and Stoltzenberg (this vol., ii, 308) for obtaining larger yields of carbon suboxide offers so few advantages over his original method as to be scarcely worth while employing.

J. C. W.

The Ternary System, H_2O–K_2SiO_3–SiO_2.—George W. Morey and C. N. Fenner (*J. Amer. Chem. Soc.*, 1917, **39**, 1173—1229).—The authors have studied the system H_2O–K_2SiO_3–SiO_2 over the temperature range 200° to above 1000°. The work comprised a determination (1) of the composition and properties of the various stable solid phases which can co-exist with solution and vapour within the above-mentioned temperature range; (2) of the composition of the solutions in equilibrium with the solid phases; (3) of the change in composition of these solutions with temperature; and (4) of the approximate corresponding three-phase pressures. In addition to quartz and the compounds $K_2Si_2O_5$ and $KHSi_2O_5$, the following new compounds occur as solid phases: potassium disilicate monohydrate, $K_2Si_2O_5,H_2O$; potassium metasilicate, K_2SiO_3; potassium metasilicate hemihydrate,

$$K_2SiO_3,0{\cdot}5H_2O;$$

and potassium metasilicate monohydrate, K_2SiO_3,H_2O. The experimental data are presented by means of tables and graphically by means of curves and photographs of solid models. Curves are given showing (1) the solubility relations in the binary systems H_2O–K_2SiO_3 and H_2O–$K_2Si_2O_5$; (2) the isothermal polybaric saturation curves; (3) the variation of pressure with the ratio $SiO_2:K_2O$ along the isotherms; (4) the isobaric polythermal saturation curves; (5) the $P.T$ curves of the various univariant systems; and (6) the boundary curves of the different solid phases in the ternary system. In addition, photographs are given of the

solid models showing the variation in the composition of the saturated solutions with temperature, and under the corresponding three-phase pressure, and also the variation of the composition of the saturated solutions with pressure at the corresponding three-phase temperatures. A short discussion is entered into in connexion with some of the theoretical relations governing the equilibrium in binary and ternary systems containing a volatile component, and also of the proper application of the term "solubility." J. F. S.

The Course of the Reaction between Silver and Sulphides (Hepar Test). FRIEDRICH L. HAHN (*Zeitsch. anorg. Chem.*, 1917, **99**, 118—122).—The blackening of metallic silver by hydrogen sulphide or soluble sulphides, used as a qualitative test for sulphur, is sometimes represented as taking place in the absence of air, with liberation of hydrogen, and sometimes as a reaction with oxygen, the former hypothesis being adopted in most recent text-books.

When precautions are taken to exclude air, silver may be boiled for hours with sodium sulphide solution without evolution of hydrogen, the metal being unchanged, blackening taking place immediately air is admitted. Hydrogen sulphide may also be passed through water in which silver is placed without any blackening. The presence of oxygen or hydrogen peroxide causes immediate blackening. C. H. D.

Properties of Barium Sulphate. Z. KARAOGLANOW (*Zeit. anal. Chem.*, 1917, **56**, 225—246).—See this vol., ii, 387.

Contamination of Precipitates in Gravimetric Analysis. Solid Solution and Adsorption versus Higher Order Compounds. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1917, **39**, 1152—1173).—A number of experiments have been carried out on the nature of the material carried down with the precipitate when sulphuric acid or sulphates are treated with barium chloride in the presence of ferric iron. In all cases it is shown that considerable quantities of iron are included in the precipitate; of the various hypotheses which have been put forward to account for such inclusions, the author, from the results of the experiments, favours the view that an insoluble complex ferric barium sulphate is formed, so that there is neither adsorption of ferric compounds nor the formation of solid solutions, but rather the formation of barium ferric sulphate, $Ba[Fe(SO_4)_2]_2,nH_2O$, which is insoluble and admixed with the barium sulphate. Although disulphatoferric acid and its alkali salts are known, attempts, which are described in the paper, to prepare the alkaline earth salts of this acid failed. J. F. S.

Example of a Reversible Reaction and Complex Salt Formation. K. ELBS (*Zeitsch. Elektrochem.*, 1917, **23**, 147—148).—A series of experiments is described to show that the reaction $CuI_2 \rightleftarrows CuI + I$ is really a reversible reaction. The reaction can

be made to proceed entirely from left to right by removal of the iodine with thiosulphate, that is, the change $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}$ is complete. If the cupric ions are removed, it is obvious that the reaction must proceed from right to left; this may be achieved by adding to the mixture of cuprous iodide and iodine a salt which forms complexes with the cupric ion. Ammonium oxalate serves this purpose, and if ammonium oxalate is added to the mixture of cuprous iodide and iodine, an intensely blue solution of cupric ammonium oxalate is formed. J. F. S.

Influence of the Velocity of Cooling on the Temperature of Transformation and Structure of Carbon Steels. A. PORTEVIN and GARVIN (*Compt. rend.*, 1917, **164**, 885—888).—For a given steel and a given initial temperature of tempering, the lowering of the transformation point is not parallel to the increase in the velocity of cooling. The transformation, well marked at high temperatures on the curve, disappears suddenly at low temperatures, and then can only be observed by comparison with a metal having no transformation point. There are thus critical values for the velocity of cooling which mark the change in the position and the form of the transformation. With transformation at high temperatures troostite is obtained, and at low temperatures martensite. In steels other than the eutectic, the troostite is always accompanied by some proeutectic constituent. When troostite and martensite exist simultaneously, the curve shows an irregularity both at high and low temperatures. A rise in the initial temperature for given conditions of tempering tends to displace the transformation at low temperatures. The critical value of the velocity of cooling for a given initial temperature depends on the composition of the steel. It does not always vary in the same sense as the carbon content, and appears to have a minimum at the eutectic content. W. G.

Anomaly of Cementite in Carbon Steels, Annealed, Tempered, and Half-tempered. P. CHEVENARD (*Compt. rend.*, 1917, **164**, 1005—1008).—The magnetic transformation of the cementite in carbon steels (compare Wologdine, A., 1909, ii, 374) is accompanied by a change in direction of the dilatation curve. Measurements have been made on nine steels, and the differential curves obtained show an irregularity of negative expansion comparable with the negative anomaly of the ferronickels of the group Fe_2Ni. For all the steels, the transformation point was at 210°, which coincides with the temperature of sudden fall of magnetisation of cementite obtained by Honda and Tagaki (compare A., 1916, ii, 105). A study of this irregularity of the cementite can be used to determine the state of the carbon in steels after treatment, and the method has been applied to a steel containing 0·83% carbon tempered at 800° in cold water. W. G.

Iron and Boron. N. TSCHISCHEVSKY and A. HERDT (*Rev. Soc. russe Met.*, 1915, **1**, 533—546; from *J. Soc. Chem. Ind.*, 1917, **36**, 650).—Iron–boron alloys containing up to 11·54% of the latter

were prepared from pure Swedish iron and ferroboron, and their cooling curves determined. For micrographic determinations, the specimens were cooled slowly and etched with a solution of sodium picrate. The eutectic alloys presented the appearance of pearlite (boron–pearlite) to a greater degree than the corresponding carbon steels. With 0·08% boron, continuous masses of ferrite were exhibited surrounded by thin lines of pearlite; the latter gradually widened and extended as the boron content increased until the eutectic composition and the maximum of pearlite were reached with 3·1% of boron. With 3·5% of boron, the formation of prismatic boride crystals (boron–cementite) commenced; these increased with the boron content, and finally agglomerated into masses separated by veins of eutectic. Polished sections of alloys containing more than 8% of boron were prepared only with difficulty, owing to general brittleness and lack of cohesion. The 8·85% alloy consisted of a mass of long, prismatic crystals of the composition Fe_2B. The results of the chemical, thermal, and micrographic analyses are shown in a diagram. H. W.

Explosive Property of Uranyl Nitrate. II. ARNO MÜLLER (*Chem. Zeit.*, 1917, **41**, 439. Compare A., 1916, ii, 143).—In order to elucidate the apparently arbitrary conditions under which explosive specimens of uranyl nitrate may be formed, ethereal solutions containing free nitric acid or nitric oxide, or without added agent, have been allowed to crystallise while under the influence of the Röntgen rays, but no effect on the crystals could be observed. The conclusion is therefore drawn that it is not the accidental presence of radium which imparts the explosive property to uranyl nitrate. J. C. W.

Preparation of Black Oxide of Uranium (UO_2). CHARLES L. PARSONS (*J. Ind. Eng. Chem.*, 1917, **9**, 466—467).—Black uranium oxide was prepared on a technical scale by fusing 35 parts of sodium chloride, 20 parts of sodium uranate, and 1 part of powdered charcoal in a cast steel pot. Reaction occurs at a red heat, and is allowed to continue until the escape of gas ceases. The cooled mass was lixiviated with water, and the heavy uranium oxide settled on the bottom of the tank and was washed by decantation. It may be freed from iron and aluminium compounds if necessary by treatment with 5% hydrochloric acid, and in commercial practice a purity equivalent to 97% U_3O_8 is easily obtained. Vanadium, if present, is recovered as a by-product, going into solution as sodium vanadate, and being precipitated therefrom by ferrous sulphate. In general, no attempt was made to separate all the iron, since its presence was not deleterious in the production of ferro-uranium. G. F. M.

The Preparation in a Pure State of Highly Reactive Metals and Metalloids. EMIL PODZUS (*Zeitsch. anorg. Chem.*, 1917, **99**, 123—131).—For the preparation of titanium and zirconium, a steel bomb is used, closed by a strong screw and

sealed with molten lead. The reduction mixture, consisting of sodium and titanium chloride or potassium zirconifluoride, is introduced in an atmosphere of hydrogen or carbon monoxide, several clean iron balls being added. The bomb being closed, the whole is revolved for twenty to forty hours at about 200° to bring about an intimate mixture. Heating strongly for a few minutes starts the reaction. When a large excess of sodium is used, vapour may escape through the lead seal. The bomb is cooled from the top downwards, so that the lead may be solid before the pressure falls. The element is obtained in a minutely crystalline, highly reactive form, titanium being 99·7% and zirconium 99·3%. The method fails to give pure boron.

Apparatus is described for the preparation and purification of boron trichloride. Reduction with sodium, even in a vessel of pure boron nitride electrically heated by a resistance spiral of boron and boron carbide, yields only a black powder which will not weld to a compact mass. Iron is found to give the best results. Wire, prepared by drawing down Kahlbaum's pure iron, is wound on a frame made of boron nitride, and heated by means of a resistance tube of boron and boron carbide enclosed in a large glass vessel with mercury seals. The leading-in wires are of tungsten. After filling with hydrogen, the furnace is heated to redness to remove traces of oxygen. Hydrogen is then expelled by filling with boron trichloride. Most of the reduction takes place at about 800°, and the temperature is then raised gradually to 1700°. A porous mass of pure boron is thus obtained, which becomes denser on prolonged heating in boron trichloride. Compact boron thus prepared has an appreciable conductivity and is very infusible, an arc struck between boron poles showing no trace of fusion unless iron is present. The wires may be heated electrically to bright whiteness without injury. C. H. D.

The Zirconyl Sulphates. ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 946—949. Compare this vol., ii, 322).—The author gives graphic formulæ showing the six zirconium sulphates as derivatives of the zirconyl radicle, which he considers them to be. The various hydrates of these sulphates are tabulated. W. G.

Double Salts of Bismuth Trichloride and Chlorides of Bivalent Metals. R. F. WEINLAND, A. ALBER, and J. SCHWEIGER (*Arch. Pharm.*, 1916, **254**, 521—536).—Bismuth chloride, prepared from the hydrated nitrate, is dissolved in the smallest possible quantity of concentrated hydrochloric acid, and the solution is treated with the carbonate or hydroxide, or in a few cases the chloride of the bivalent metal. The latter was added in some cases so long as it dissolved, in other cases in amounts less than this. In no case did the solution of bismuth chloride (1 mol.) dissolve more than 1 mol. of the bivalent chloride. The solutions were then concentrated over sulphuric acid until the double salts crystallised. The double salts obtained are colourless (except when a coloured cation has been added), hygroscopic, and are decom-

posed by water, bismuth oxychloride being precipitated. Three series of salts have been obtained: (1) $BiCl_3,M''Cl_2$, obtained when the solution of bismuth chloride has dissolved the maximal amount of carbonate or hydroxide. Such salts are: $M''=Mg$, stout, rectangular plates with $8H_2O$; $M''=Ca$, plates with $7H_2O$; $M''=Sr$, rectangular, four-sided plates with $8H_2O$; $M''=Ba$, rhombic plates with $4H_2O$; $M''=Co$, pale red prisms with $6H_2O$; and $M''=Ni$, green needles with $6H_2O$. These salts correspond with the series $BiCl_3,2M'Cl$, where M' is an alkali metal, and are regarded as derivatives of pentachlorobismuthic acid, $H_2[BiCl_5]$. (2) $2BiCl_3,M''Cl_2$, obtained generally from solutions in which the molecular ratio of bismuth chloride to bivalent chloride is 10:4 or 10:2. Such salts are: $M''=Ca$, colourless needles with $7H_2O$; $M''=Sr$, stout needles with $7H_2O$; and $M''=Ba$, slender needles with $5H_2O$. They correspond with the series $BiCl_3,M'Cl$ (M'=alkali metal), and are regarded as derivatives of tetrachlorobismuthic acid, $H[BiCl_4]$. (3) $4BiCl_3,M''Cl_2$, obtained generally when the molecular ratio of bismuth chloride to bivalent chloride is 10:1. Such salts are: $M''=Mg$, six-sided leaflets with $16H_2O$; $M''=Sr$, six-sided leaflets with $12H_2O$; $M''=Mn$, flesh-coloured, six-sided plates with $12H_2O$; $M''=Fe$, faintly yellowish-red plates with $12H_2O$ (the colour is probably modified by the presence of a little ferric salt); $M''=Co$, red, six-sided plates with $12H_2O$; and $M''=Ni$, pale green, six-sided plates with $12H_2O$. These salts correspond with the series $2BiCl_3,M'Cl$ (M'=alkali metal), and are regarded as derivatives of heptachlorodibismuthic acid, $H[Bi_2Cl_7]$.

The distribution of the water in the double salts is discussed from the point of view of the co-ordination theory. C. S.

Colloidal Metals of the Platinum Group. IV. Colloidal Iridium. C. PAAL (*Ber.*, 1917, **50**, 722—737. Compare A., 1904, ii, 180).—Directions are given for the preparation of iridium hydrosols which may be safely dried, by reduction of alkaline iridium solutions with hydrogen, hydrazine hydrate, sodium formate, or formaldehyde, in the presence of sodium protalbate or lysalbate as protective colloid.

Technical iridium chloride, which is the available starting material, is a mixture of the tetrachloride with some trichloride. It is slightly hydrolysed by water, and clear solutions are only obtained by the addition of hydrochloric acid. When the solution is added to solutions of the protective colloid, olive-green or rust-brown precipitates of the protalbate or lysalbate are produced, the colour being dependent, apparently, on the amount of free hydrochloric acid. These precipitates dissolve in sodium carbonate or hydroxide to form the blood-red hydrosols of iridium trihydroxide. With an excess of sodium hydroxide, the sol suffers oxidation on exposure to the air, giving the blue hydrosol of iridium tetrahydroxide. The iridium hydrosols obtained from these by reduction are of different degrees of sensitiveness towards electrolytes. With sodium formate or formaldehyde, the un-

dialysed hydroxide sols may be safely used, but dialysis must precede any application of hydrazine as the reducing agent or any attempt to prepare concentrated iridium sols. If the sol with sodium lysalbate as the protective colloid is acidified, some of the lysalbic acid is left in solution and the gel therefore enriched in iridium. By redissolving this in sodium hydroxide and repeating the process a few times, a sol may be obtained which, on drying, contains as much as 73% of iridium.

The solutions employed contain 1% of iridium as chloride and 1% of the protective salts. During the final dialysis, a small quantity of alkali is lost, owing to the hydrolysis of the protective salts, so it is advisable to replenish this before evaporating the sol.

[With FERD. BIEHLER and HERMANN STEYER.]—The reduction with sodium formate in the presence of sodium protalbate and lysalbate is described. The dry preparations formed black, glistening, friable lamellæ, which redissolved almost completely after a year or so, and contained from 30—42% of iridium.

[With HERM. STEYER.]—Reductions with formaldehyde, hydrazine hydrate, and gaseous hydrogen are described. J. C. W.

Mineralogical Chemistry.

Palæophysiology: the Organic Origin of some Minerals Occurring in Sedimentary Rocks. J. V. Samoilov (*Min. Mag.*, 1917, **18**, 87—98).—In connexion with the exploration of the phosphate deposits of Russia, the occurrence of barytes has been noted over a wide area in the governments of Kostroma, Kazan, and Simbirsk, whilst still farther to the north-east similar deposits of barytes have been met with in the basin of the Pechora River. The mineral occurs as nodules in the clays and marls of the Upper Jurassic, and is confined to the Oxfordian-Sequanian horizon, though in some of the districts it extends up into the Kimeridgian. Nodules of barytes have been dredged from the sea-floor off the coast of Ceylon, and granules of barium sulphate have been detected in the bodies of certain marine organisms, namely, the Xenophyophora. If, therefore, during the Upper Jurassic period such organisms, capable of extracting barium salts from sea-water, were more abundant, they would account for the accumulation of barium in these strata, where the barytes occurs as a primary mineral.

Similarly, the mineral celestite has been found over a very wide area in Turkestan in beds of Upper Cretaceous age. The presence of strontium sulphate has been detected in the skeletons of the Acantharia, a group of the Radiolaria. It is conceivable

that similar organisms were relatively more abundant during the Cretaceous period, and that their remains gave rise to the deposits of celestite.

Although the iron compound hæmoglobin plays an important function in the blood of present-day animals, yet cases are known amongst the Crustacea and Mollusca in which the copper compound hæmocyanin performs the same function; and vanadium has been detected in the blood of the Ascidia. During former periods of the earth's history these, and perhaps some other, metals may have predominated in the blood of animals then living. In this connexion, the persistent occurrence in the Permian strata of copper minerals and ores associated with abundant animal remains is significant. In the same way there may have been at different periods variations in the chemical composition of the ash of plants.

The recurring presence of minerals of primary origin in certain sedimentary strata therefore suggests that there may have been varying physiological processes during past periods, and for this new branch of palæontology the name palæophysiology is suggested.

L. J. S.

Cyanotrichite and Dioptase from Traversella. LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 487—491).—Small stalactites and thin incrustations coating some of the rock in a gallery of one of the Traversella mines were found to consist of either very thin plates aggregated so as to form a radiating structure about the axis of the stalactites or minute acicular crystals which tend towards a lamellar habit when their dimensions increase. Both the plates and needles are colourless under the microscope, but thicker aggregates exhibit a greenish-blue colour with no trace of pleochroism. They contain a little calcium, apparently as contamination in the form of gypsum, and if an allowance is made for this, the percentage composition is as follows:

CuO.	Al_2O_3.	SO_3.	H_2O (by diff.)
53·05	8·72	12·11	26·12

The mineral is hence a variety of cyanotrichite, differing from other minerals known as cyanotrichite and woodwardite in its high content of water and its poorness in aluminium.

The stalactites also contain isolated individual masses or dendritic forms of an emerald-green mineral, which forms moderately hard, prismatic crystals, and appears to be dioptase.

T. H. P.

Tapiolite from Western Australia. EDWARD S. SIMPSON (*Min. Mag.*, 1917, **18**, 107—121).—Crystals of tapiolite ($FeTa_2O_6$) are described from Tabba-Tabba Creek and from Greens Well, in the Pilbara goldfield. They are tetragonal ($a:c=1:0·6539$), and by twinning simulate monoclinic symmetry. The density of different crystals ranges from 7·36 to 7·907; the latter value, being the highest recorded, is assumed to represent the density of pure iron tantalate (the value for the corresponding columbate, mossite,

being set at 5·20). Analysis of a crystal (D 7·45) from Tabba-Tabba Creek gave:

Ta_2O_5.	Cb_2O_5.	TiO_2.	SnO_2.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
82·55	1·37	0·18	0·34	0·83	10·69	1·49	1·96	0·10	0·31	99·82

L. J. S.

Magnesian Tourmaline from Renfrew, Ontario. E. L. BRUCE (*Min. Mag.*, 1917, **18**, 133—135).—Reddish-brown crystals and grains occur in limestone and in granite-gneiss near the contact of the two rocks in a limestone quarry near the town of Renfrew. The mineral encloses much graphite and calcite; analysis of carefully selected material, D 3·07, gave:

SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	TiO_2.	CaO.	MgO.	K_2O.	Na_2O.	F.	H_2O.	Total less O for F.
35·29	10·56	28·93	2·35	0·70	0·025	5·49	14·53	0·22	1·72	0·84	0·70	101·00

These results agree with the formula $H_{18}(BOH)_2Si_4O_{19}$ of Penfield and Foote (A., 1899, ii, 304). L. J. S.

Composition of Pyroxenes. C. DOELTER (*Centr. Min.*, 1917, 185—191).—A criticism of the recent papers by Boeke (A., 1911, ii, 283), Zambonini (A., 1915, ii, 570), and Tschermak (A., 1916, ii, 145). Little definite evidence can be adduced either for or against the various hypothetical components assumed by these authors. Further experimental work is needed in the direction of the preparation of possible components and their miscibility.

L. J. S.

Analytical Chemistry.

Simple Device for Evaporating Solutions to a Definite Volume. G. P. Plaisance and N. C. Pervier (*J. Amer. Chem. Soc.*, 1917, **39**, 1238—1241).—A device is described by which a number of solutions may be evaporated to any required volume without any attention. The apparatus works on the principle of a balance; a plate of metal perforated with nine holes of slightly larger diameter than a beaker is hung from a pair of metal rods. The rods work on knife edges supported by a metal stand, and are balanced at the far end by weights. The beakers, of the same size, are filled with the same volume of liquid and rest on a hot-plate or water-bath; suitable weights are placed on the other arm. When sufficient of the liquid has evaporated, the beakers are raised from the hot-plate by the weights and brought against a large glass slab, which serves the double purpose of covering the beakers and preventing them being raised too much. J. F. S.

Apparatus for the Reduction of Volume of Gases to Standard Temperature and Pressure. A. V. C. FENBY (*Chem. News*, 1917, **116**, 5—8).—A mechanical device designed to facilitate the reduction of the volumes of gases, measured at known temperatures and pressures, to normal temperature and pressure. Three different forms of the instrument are described, one of these being of the ordinary slide-rule pattern and one a circular form.

H. M. D.

Improved Compensator for Gas Analysis. E. T. GREGG (*J. Ind. Eng. Chem.*, 1917, **9**, 528).—An improved compensator is described for use in conjunction with the Hempel apparatus to adjust the pressure of the gas in the burette before taking a reading. It depends on the making of a mercury platinum contact in a U-shaped manometer connected with the burette on the one hand and a compensator bulb on the other. The contact forms part of a circuit in which are included a small dry cell, a switch, and a miniature lamp, and the volume of the gas in the burette is adjusted by means of a mercury levelling bottle until the lamp glows. It is claimed that this arrangement gives more accurate results in less time and with less strain on the eyes of the operator than the usual optical method of adjusting the mercury to a mark.

G. F. M.

Titration of Chlorides by Mohr's Method, and its Application to the Examination of Potable Water. I. M. KOLTHOFF (*Pharm. Weekblad*, 1917, **54**, 612—618).—The best proportion of chromate in the titration of chlorides is 0·7—1 c.c. per 100 c.c. of liquid. The end-point is more readily observed in artificial light than in daylight. The presence of free acid, phosphates, and ferrous and ferric salts interferes with the sensitiveness of the reaction, but borax has no effect. A. J. W.

Volumetric Estimation of Sulphur in Pyrites. HARCOURT PHILLIPS (*Chem. News*, 1917, **115**, 312).—A description of a rapid method for the estimation of sulphur in pyrites, based on the use of a standard solution of barium chloride, of which 1 c.c. is equivalent to 0·01 gram of sulphur. A deficient quantity of barium chloride solution is added to the oxidised pyrites solution which has been freed from nitric acid and has been adjusted to a definite bulk; the titration is completed by making further additions of 0·5 c.c., boiling the liquid, and filtering off 5 c.c. after each addition, the end-point being reached when this hot filtrate fails to give a turbidity in three minutes after the addition of two more drops of the barium chloride solution.

The barium chloride solution is standardised under similar conditions against a solution of sulphuric acid made to contain the equivalent of 0·01 gram of sulphur per c.c. D. F. T.

Detection and Estimation of Sulphur in Petroleum. C. K. FRANCIS and C. W. CRAWFORD (*J. Ind. Eng. Chem.*, 1917, **9**, 479—481).—E. Fischer's methylene-blue test provides the most

delicate method for the detection of sulphur in petroleum. The sulphur is converted into sodium sulphide by treating the oil with sodium in the usual way, and in the filtered solution, slightly acidified with hydrochloric acid, a crystal of *p*-aminodimethylaniline sulphate is dissolved. A few drops of ferric chloride solution are then added, and the formation of a blue coloration indicates the presence of sulphur. No sulphur as hydrogen sulphide or carbon disulphide was found in the Cushing oil (Bartlesville sand), but alkyl sulphides and thiophens were present. Hydrogen sulphide was formed when the oil was heated above 225°. For the quantitative estimation of sulphur, the Eschka method was not applicable, but by fusion with sodium peroxide and potassium chlorate in a bomb and estimation as sulphate, accurate results were obtained. A modified Dammer combustion method (*Zeitsch. angew. Chem.*, 1911, **22**, 400), using catalytic oxidation with platinum spirals and absorption of the oxides of sulphur in hydrogen peroxide, also gave concordant results, but required greater care and vigilance than the peroxide method. G. F. M.

The Use of Potassium Persulphate in the Estimation of Total Nitrogen in Urine. LEONARD C. SCOTT and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1044—1051. Compare Huguet, A., 1910, ii, 155).—A comparison of the macro- and micro-chemical methods of estimating total nitrogen in urine, replacing potassium sulphate by the persulphate, free from nitrogen. In the macrochemical method, 5 c.c. of the urine, 10 c.c. of sulphuric acid, and 10 c.c. of a 2·5% solution of copper sulphate are boiled until the liquid is yellow. The flask is allowed to cool and 1·5—2·0 grams of potassium sulphate added, and the liquid reheated until the action begins. The flask is removed from the flame and rotated until the solution is colourless, being finally reheated until all sulphur trioxide is driven off. The estimation of nitrogen is then made as in the ordinary Kjeldahl process. In the microchemical method, the procedure recommended by Folin and Farmer (compare A., 1912, ii, 702) is followed, using the persulphate instead of the sulphate, and finally driving off all the sulphur trioxide as above. Both these methods are rapid and yield results which agree with those obtained by the Arnold-Gunning method taken as a standard. In the micro-method, all traces of calcium and magnesium must be eliminated from the water used for the dilutions. W. G.

Estimation of Ammonia in the Soil and in Liquid Manure. W. J. BARAGIOLA and O. SCHUPPLI (*Landw. Versuchs-Stat.*, 1917, **90**, 123—137).—The ammonia present in the soil may be estimated as follows: 50—100 grams of the soil are mixed with 5—7 grams of magnesium oxide, and at once introduced into a Claisen (two-necked) fractionating flask holding about three-quarters of a litre, together with about 100 c.c. of water. The

flask is connected with a bulbed tube passing tightly through the stopper of a pump flask which contains 10—20 c.c. of $N/5$-sulphuric acid, and is surrounded by ice-water. The side-tube of the pump flask is connected with that of a second, which serves as a safety flask, and is joined to a water-pump and also carries a manometer. A tube drawn out at the bottom to a capillary and connected above with a sulphuric acid washing bottle passes almost to the bottom of the distillation flask.

The pressure is lowered to about 15 mm. and the water-bath in which the distillation flask is immersed heated to about 35°. The distillation is continued until the residue is dry, this requiring about two hours. A slow current of ammonia-free air is then passed for a time through the flask. The contents of the receiver are finally washed out into an Erlenmeyer flask, boiled to expel carbon dioxide, and when cold titrated with $N/10$-sodium hydroxide in presence of Congo-red; the titration is carried on until the colour matches that given by a mixture of the same volume of $N/5$-sulphuric acid as is used in the test with an equivalent volume of $N/10$-sodium hydroxide.

Under the above conditions, not only ammonia, but also volatile amines and other bases, pass over, and the ammonia may be separated in the following manner. Either a fresh distillate, obtained as above, or an aliquot part of the original distillate before addition of Congo-red, is treated in a beaker with 1 c.c. of concentrated hydrochloric acid and 10 grams of sodium acetate and 12 grams of sodium phosphate dissolved in the liquid; the sparingly soluble phosphate may with advantage be dissolved separately in a little hot water and the cooled solution added to the liquid. After further addition of 15 c.c. of 10% magnesium chloride solution, a little phenolphthalein, and a pinch of quartz sand, the whole is vigorously stirred mechanically by means of a water-turbine. Sodium hydroxide solution is slowly added from a dropping funnel until a persistent, faint pink coloration is reached. After about fifteen minutes, the amorphous, gelatinous precipitate assumes a crystalline form, the pink colour disappearing. A further addition of sodium hydroxide solution is made until the liquid again remains pink, and the liquid then kept stirred for fifteen minutes longer. If too much sodium hydroxide is accidentally added and danger of decomposition of the magnesium ammonium phosphate into trimagnesium phosphate and ammonia thus incurred, hydrochloric acid should be added and then the alkali until the proper end-point is reached. The stirring should last altogether about half an hour. The solution is allowed to settle for a short time and then filtered through a Neubauer platinum crucible or a porcelain Gooch crucible, the heavier quartz sand being left in the beaker and subsequently washed, together with the precipitate on the filter, with a total of about 25 c.c. of 3% sodium acetate solution. The precipitate adhering to the sand and also that on the filter is dissolved in dilute hydrochloric acid, the solution being afterwards distilled with excess of sodium hydroxide solution and the ammonia collected in standard sulphuric

acid and estimated by titration with sodium hydroxide in presence of Congo-red.

The ammonia which passes over when soil is distilled with magnesium oxide seems to be that actually existing as ammonium salts in the soil, since after some time it disappears, having undergone complete conversion into nitrate.

The above method is applicable also to liquid manure, 50 c.c. of the latter and 10 grams of magnesium oxide being taken, and the distillate made up to a definite volume and aliquot portions used for the direct titration of the volatile basic nitrogen and for the precipitation of the ammonia as magnesium ammonium phosphate.

Both in soil and in liquid manure, direct titration of the distillate obtained as above and that from the magnesium ammonium phosphate gives virtually identical values, so that amines and volatile bases other than ammonia pass over only in negligible quantity. T. H. P.

A Precipitant for Nitrous Acid. FRIEDRICH L. HAHN (*Ber.*, 1917, **50**, 705—708).—2:4-Diamino-6-hydroxypyrimidine (Traube, A., 1900, i, 416) is an excellent precipitant for nitrites, giving a precipitate with as little as 0·05 mg. NO_2' per c.c., and a coloration with as little as 0·015 mg. The precipitate cannot be used for quantitative estimations of nitrites, but the process is particularly useful for detecting nitrates in nitrites. The sparingly soluble sulphate is the best salt to employ, as the excess of reagent largely crystallises out in the cold, and nitrates can then be estimated undisturbed in the filtrate by means of "nitron" or detected with the usual sensitiveness by means of diphenylamine or ferrous sulphate. J. C. W.

Application of the Gutzeit Test to Works Estimation of Arsenic. C. HOLLINS (*J. Soc. Chem. Ind.*, 1917, **36**, 576—577).—An apparatus is described and figured which has proved useful in examining the quality of dearsenicated vitriols, and is also applicable to the estimation of arsenic in phosphates, phosphoric acid, and other substances containing only small quantities of arsenic. It consists of a wide-mouthed bottle of about 100 c.c. capacity fitted with a two-holed rubber bung. One hole supports a short tube bent at right angles and closed by a cap; the other supports a tube of 4—5 mm. internal diameter on which three bulbs are blown, the first two of which contain a little lead acetate solution (10—20%), whilst the third is tightly packed with glass wool wetted with the same solution; the third bulb is connected to a tube inclined at an angle of 45°, which contains the mercuric chloride paper (10 cm. long). The latter is best prepared by soaking Michallet drawing paper in water until limp, and then keeping it moving in mercuric chloride solution (1%) for half an hour. The sheets are drained and dried separately in the steam-oven. They can then be preserved for two or three months in the dark in a test-tube fitted with a rubber bung.

A series of standard stains is prepared with known amounts

of arsenic. These are trustworthy for about three months if preserved with phosphoric oxide in sealed tubes and exposed to light as little as possible. The sensitiveness of a new batch of papers must, however, always be tested by preparing two or three standards from it.

In performing the test, 40 c.c. of water are placed in the flask, a measured volume of the vitriol (0·5—2·0 c.c.), and sufficient arsenic-free sulphuric acid to make up the total acid to 2 c.c. (D 1·84) are added. Three drops of arsenic-free stannous chloride solution are introduced, the paper slip is placed in the tube, and 3—4 grams of arsenic-free zinc are added. After half an hour the stains are compared with the standards.

The most accurate results with 1% mercuric chloride paper are given by stains of between 7 and 20 micromilligrams. With stains of 35 or less, there is no loss of arsenic hydride. Under certain conditions of dilution, appreciable quantities of hydrogen sulphide are evolved, but the test is trustworthy if the glass wool is not blackened. The time occupied by a single estimation is less than thirty-five minutes.

A stain which is otherwise invisible may be developed by touching the paper with a drop of concentrated hydrochloric acid. A stain which is just visible on development represents about 0·05 micromilligram of arsenious oxide.

The sensitiveness of the test paper is diminished by using concentrated solutions of mercuric chloride, but does not increase on dilution beyond 0·5%. Paper prepared with 1% solution is nearly three times as sensitive as that prepared with a saturated solution.

H. W.

The Estimation of Boric Acid in Special Glasses. PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1917, [iv], **21**, 97—101).—Slight modifications are introduced into the method of Hönig and Spitz (compare A., 1917, ii, 159). It is necessary to exclude all carbon dioxide from the solutions prior to titration in the presence of glycerol or mannitol with phenolphthalein as indicator, and all ammonium salts must be driven off. Magnesium and aluminium, in amounts greater than those which exist in special glasses, do not interfere with the estimation or retain any boric acid.

Provided that the material is first thoroughly fused with alkalis, the method of estimating boron, by distillation as methyl borate, is satisfactory. W. G.

Experiences with Mandel and Neuberg's Catalytic Method for Elementary Analysis. TH. MERL and K. LÜFT (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 384—388).—The authors describe the application of Mandel and Neuberg's method (oxidation with 15% hydrogen peroxide in the presence of a small quantity of iron. A., 1915, ii, 788) to the estimation of sulphur in "saccharin" and bromine in the bromine derivatives of higher fatty acids, and find it most satisfactory. The method also serves

well as a preliminary test for "saccharin" on the ether–light petroleum extract obtained in a systematic analysis. Within a few minutes it is possible to obtain from less than a milligram of the substance distinct evidence of the oxidation products, sulphuric acid, ammonia, and benzoic acid. J. C. W.

The Analysis of Coal, and a New Scheme for the Examination of Coal. H. Gröppel (*Chem. Zeit.*, 1917, **41**, 413—414, 431—434).—The author discusses the methods which have been used and are now in common practice for estimating moisture, yield of coke or volatile products, and ash in coal, and directs attention to their respective merits and failings.

A new procedure is recommended, in which the moisture, coke, and ash are estimated with the same weight of coal in the same apparatus, a bent, hard glass tube ("duck"-shaped). For the estimation of moisture, the tube is connected to weighed calcium chloride tubes, the bend is immersed in a bath at 105°, and dry hydrogen is passed through. After removing the drying tubes, the coal is then coked in the current of hydrogen, and finally burnt in a stream of oxygen for the ash determination. As an alternative, the combustion tube may be sealed to a tube bent into two parallel U's, the second of which is filled with glass beads. With this, the dried coal is coked and the tar and water absorbed in the bent tubes, which are cooled. The coking tube is then severed, and so the weights of coke and of tar + water, and consequently of gas, can be obtained. J. C. W.

The "New" Method of Gad-Andresen for Estimation of Carbon Monoxide in the Blood. N. Zuntz (*Biochem. Zeitsch.*, 1916, **78**, 231—232).—The method described by Gad-Andresen (A., 1916, ii, 447) does not differ in essentials from that previously described by the author and J. Plesch (*Biochem. Zeitsch.*, **11**, 47). S. B. S.

Apparatus for Estimating the Noble Gases [Argon, etc.] and Nitrogen by a Gas-analysis Method. R. Brandt (D.R.-P., 296115; from *J. Soc. Chem. Ind.*, 1917, **36**, 616).—A mixture of argon, etc., with nitrogen, hydrogen, oxides of carbon, methane, and such gases, is treated in a tube connected with a manometer and a two-way tap, with metallic calcium in the form of large crystals, or with alloys of calcium with magnesium and aluminium, and with calcium nitride. The former absorbs all nitrogen and the latter hydrogen, methane, etc., at temperatures between 200° and 650°. H. W.

Estimation of Potassium. The Lindo-Gladding Method. P. L. Hibbard (*J. Ind. Eng. Chem.*, 1917, **9**, 504—513).—A study was made of the Lindo-Gladding method for the estimation of potassium, particularly from an agricultural chemical point of view, and the following are the more important observations made. The solution is preferably made by

extraction with hot water on a tube filter. The volume of water used, the excess of ammonia, and time of keeping before filtering are immaterial. The ammonia should be added before the ammonium oxalate, and if there is more than enough phosphate present to precipitate the bases, the oxalate should not be used at all, unless, as when a great excess of soluble phosphate is present, calcium chloride is previously added in slight excess to precipitate this. Occlusion of potassium salts in the gelatinous calcium phosphate must be guarded against either by reprecipitation or by greater dilution of the original solution. In igniting the salts with sulphuric acid, the temperature must be kept below the fusion point until all the carbon is burned off. The residue is dissolved in dilute hydrochloric acid, the silica filtered off, and the solution diluted to such an extent that on the addition of platinic chloride no immediate precipitation occurs. The solution is then evaporated until it is pasty, but not dry; it should be kept just acid with hydrochloric acid, and excess of platinic chloride should be avoided if much sodium is present. The purification of the potassium platinichloride is usually completed by five or six washings with 10 c.c. of 80% alcohol, and it is best collected in an ordinary Gooch crucible and dried for an hour at 120°. The perchlorate method for the estimation of potassium is longer, more difficult, and more expensive than the platinum method.

G. F. M.

Estimation of Potassium and Sodium in the Form of Sulphates by Platinum Chloride. (MLLE.) BRONISLAVA TURKUS (*Ann. Chim. anal.*, 1917, **22**, 101—102).—The mixed sodium and potassium sulphates are weighed and dissolved in water, and to the solution the calculated quantity of platinum chloride and a little hydrochloric acid are added in small portions, the solution being evaporated to dryness between each addition. The sodium platinichloride is removed by washing the precipitate with 85% alcohol, and the potassium platinichloride dried and calcined. The residual platinum is washed, dried, ignited, and weighed. The sodium is estimated by difference. W. G.

Estimation of Sodium Sulphide in Sulphide Dyebaths. H. SWANN (*J. Soc. Dyers*, 1917, **33**, 146—148).—A rapid method based on the conversion of sodium sulphide into ammonium sulphide, and the distillation of this into a known volume of standard iodine solution acidified with acetic acid.

Fifty c.c. of the dye liquor are diluted to 250 c.c., and 20 c.c. of this liquid are transferred to a conical flask. To this liquid 10—20 c.c. of a 25% solution of ammonium chloride are added, and the mixture is distilled for not more than five minutes into 25 c.c. of $N/10$-iodine solution diluted with 100 c.c. of water and acidified with acetic acid. The excess of iodine is titrated with $N/10$-thiosulphate solution, using starch as an indicator. One c.c. of $N/10$-iodine solution = 0·012 gram of sodium sulphide, $Na_2S,9H_2O$. Thiosulphates, carbonates, and sulphates have no influence on the

estimation. In the presence of sulphide dyestuffs, results are obtained varying with the amount of dyestuff present. In the presence of sulphite, results were obtained varying with the amount of sulphite present, owing to a reaction which was not further investigated. W. G.

Estimation of the Alkalinity and Phosphoric Acid Content of the Ash of Feeding Stuffs. I. M. KOLTHOFF (*Chem. Weekblad*, 1917, **14**, 547—558. Compare A., 1916, ii, 538; Pfyl, A., 1914, ii, 290).—The author does not consider that Pfyl's method for estimating the alkalinity of the ash of foods possesses any advantage over his own. A. J. W.

New Applications of Thymolphthalein and Naphtholphthalein in the Estimation of True Neutrality in Waters, including Rapid Methods for Analysing Limestone and Ammonium Salts. J. MOIR (*J. Chem. Met. and Min. Soc. S. Africa*, 1917, **17**, 129—132; from *J. Soc. Chem. Ind.*, 1917, **36**, 571). —The insensitiveness of thymolphthalein to traces of alkali, particularly in boiling solutions, has been utilised in the estimation of lime and magnesia in limestone; 0·5—0·75 gram of the sample, free from grit, is mixed with about 10 c.c. of 2*N*-hydrochloric acid, the mixture heated on the water-bath for about twenty minutes, the turbid liquid diluted to about 20 c.c., and titrated with *N*/2-sodium hydroxide solution (free from carbonate), using a methyl-red solution (0·02%) in dilute alcohol as indicator; the combined acid equivalent of the lime and magnesia is thus obtained. After diluting to 50 c.c. and boiling for one minute, 3 c.c. of 1% thymolphthalein solution in 60—70% alcohol, and then sufficient *N*/2-sodium hydroxide to give a dark blue solution, are added, the mixture boiled for one minute to coagulate the precipitated magnesia, and the blue suspension titrated until yellow with *N*/2-hydrochloric acid; in this manner, the magnesia content is determined, and the lime may be obtained by difference. A correction should be made if an appreciable amount of phosphate is present. The results agree closely with those obtained by the ordinary method.

In analysing the ammonium salts of strong acids, the solution, previously neutralised to methyl-red if necessary, is titrated at the boiling point with *N*/5-sodium hydroxide in presence of a small quantity of a saturated solution of thymolphthalein in 50% alcohol until the deep blue to green colour reappears and withstands boiling for twenty seconds.

The true neutrality of water is estimated by using as mixed indicators methyl-red and α-naphtholphthalein, which are much more sensitive than methyl-orange and phenolphthalein, and will detect 0·1 part of sulphuric acid and 0·2 part of calcium hydroxide per 100,000. In the presence of more than 0·4 part of acid in 100,000, the colour is violet-rose; 0·2 part of acid, salmon-orange; neutral, straw-yellow; 0·2 part of alkali, citrine-green; more than 0·4 part of alkali deep bluish-green. Neutral red, rosolic acid, or alizarin may be used in place of methyl-red. H. W.

Microchemistry of Plants. V. Detection of Dissolved Calcium Compounds by means of Sodium Carbonate. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, **34**, 288—295).—One of the most sensitive reactions for the microchemical detection of calcium in plant tissue consists in treatment with concentrated aqueous sodium carbonate solution (from 10% to an almost saturated solution), which results in the precipitation of sodium calcium carbonate or gaylussite crystals. The rapidity and abundance with which the crystals are formed increase with the concentration of the sodium carbonate solution employed.

T. H. P.

Microchemistry of Plants. VI. Detection of Lime by means of Potassium Hydroxide or a Mixture of Potassium Hydroxide and Carbonate. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, **34**, 357—363).—Treatment of a plant section containing dissolved or undissolved calcium compounds with a drop of semi-saturated aqueous potassium hydroxide leads to the gradual formation of characteristic, hexagonal plates or disks, which may change later into crystalline aggregates resembling full-blown flowers. The crystals consist of the double salt,

$$2CaCO_3,3K_2CO_3,6H_2O.$$

This test is rendered more rapid and certain if the semi-saturated potassium hydroxide solution (1 vol.) is mixed with saturated potassium carbonate solution (1 vol.). The reaction takes place with calcium carbonate, sulphate, nitrate, phosphate, oxalate, malate, tartrate, acetate, or butyrate. T. H. P.

Properties of Barium Sulphate. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 225—246).—Pure barium sulphate may be obtained from the product contaminated with barium chloride by dissolving it in concentrated sulphuric acid, heating the solution for a long time, precipitating the barium sulphate by diluting with much water, and washing and drying the precipitate. Such barium sulphate does not lose in weight when heated over a Teclu burner in either a platinum or a porcelain crucible. When heated for an hour in a blowpipe flame, it is, however, diminished appreciably in weight, especially in a platinum crucible, and the resultant salt smells of hydrogen sulphide in the cold. The barium sulphide thus formed undergoes very slow oxidation when heated over a Teclu burner. In a porcelain, but not in a platinum, crucible, diminution in weight (for instance, from 1·0622 to 1·0608 gram) occurs when barium sulphate is ignited in contact with filter paper; the amount of the loss is inconstant and small, but in accurate work the dried precipitate should be separated from the filter paper and the latter burnt in another crucible.

Direct determinations have been made of the solubility of barium sulphate in water and in solutions of various acids and salts by boiling a known weight of the pure salt for two hours with 200 c.c. of a solution of the electrolyte, allowing to remain with frequent shaking for twenty-four hours, filtering, washing with 350 c.c. of water, igniting, and weighing; the amount of

barium sulphate dissolved in the washing water was determined separately and the results corrected accordingly. The solubility per litre is 0·0043 gram in pure water, or 1 in 232,558; that this solubility is considerably higher than that previously found by other investigators (1 in about 400,000) is explained by the fact that the salt used is of very fine grain and passes even through a double filter. Barium sulphate occludes barium chloride in amount depending on the concentration of the chloride, such occlusion depending on the fineness of the precipitate. The solubility of barium sulphate in sulphuric acid solutions is actually diminished or even destroyed if the concentration of the acid is higher than 0·3*N*; with lower concentrations, the solubility is almost the same as in pure water.

The solubility of barium sulphate in solutions of potassium chloride or nitrate is greater than in water, owing to double decomposition between the barium sulphate and the potassium salt; it is thus evident that, under these conditions, the barium and sulphate radicles exist in solution, not only in the ionic state, but also partly as undissociated barium chloride, barium nitrate, and potassium sulphate molecules. Potassium sulphate or a mixture of either potassium chloride and sulphate or potassium chloride and sulphuric acid also increases, but only slightly, the solubility of barium sulphate in water. Towards sodium sulphate or a mixture either of sodium chloride and potassium sulphate or of sodium chloride and sulphate, barium sulphate behaves in the same way as towards the corresponding potassium salts. Sodium chloride increases the solubility, but not with similar dependency on the concentration as with potassium chloride, and the results are not reproducible.

In 1·44*N*-calcium chloride, the weight of barium sulphate found is greater than that taken, but at lower concentrations the weight diminishes; the amount of the diminution does not, however, depend on the concentration of the calcium chloride, but is equal to the solubility of the barium sulphate in pure water. The solubility of barium sulphate, or, more accurately, its diminution in weight, is greater than in water or calcium chloride solutions; strontium chloride behaves, however, quite differently from calcium chloride, owing to the comparatively slight solubility of strontium sulphate and the consequent diminished formation of sulphate ions.

In 0·118*N*-lead nitrate solution, barium sulphate increases in weight, owing to interaction of the two salts, and consequent precipitation of lead sulphate. With lower concentrations of the lead ion, the amount of lead sulphate formed diminishes, and so also does the weight of the precipitate, a minimum being reached which corresponds with the solubility of the barium sulphate under the experimental conditions; finally, the solubility in pure water is attained.

Barium sulphate is insoluble in ferric sulphate containing sulphuric acid, and sometimes increases slightly in weight, owing to adsorption by the precipitate and filter paper. In ferric

chloride solution containing hydrochloric acid, barium sulphate exhibits marked solubility, which depends on the concentration of the ferric salt; in ferric chloride solution containing barium chloride, barium sulphate is, however, insoluble. In hydrochloric acid solutions the solubility is considerably greater than in solutions of potassium, sodium, or strontium chloride, etc., and is also greater, though not so much so, than in ferric chloride solutions; the solubility depends, indeed, solely on the concentration of the hydrogen ion. In nitric acid, barium sulphate is more soluble than in hydrochloric acid, ferric chloride, etc., but if barium chloride or sulphuric acid is also present, the precipitate is practically insoluble in nitric acid.

The solubility of barium sulphate in different electrolytes is determined by two factors, the anion and the cation. The anion, SO_4'', diminishes the solubility, NO_3' increases it, and Cl' is indifferent. Of the cations, $Ba^{\cdot\cdot}$ diminishes the solubility of barium sulphate, whilst $Ca^{\cdot\cdot}$ is indifferent, and $K^{\cdot}$, $Na^{\cdot}$, $Sr^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $H^{\cdot}$ increase it. T. H. P.

The Analysis of Zinc Alloys. MOSSBACHER (*Zeitsch. öffentl. Chem.*, 1917, **23**, 113—115).—Details are given of a rapid method for the full analysis of zinc alloys. After dissolving in concentrated nitric acid and evaporating to one-third bulk, sulphuric acid is dropped into the middle of the liquid, and heating is continued until white fumes are evolved. Water and alcohol are added, and after several hours the lead sulphate is collected. The filtrate is ignited in a crucible which has just previously been heated with a drop of sulphuric acid. Copper is precipitated as sulphide and heated with sulphur in hydrogen in a silica crucible. Aluminium and iron are precipitated from the filtrate, after removal of hydrogen sulphide, by adding hydrogen peroxide, and then, rapidly, a large excess of ammonia. By adding a little Congo-red, that part of the colloidal precipitate which always adheres to the glass is made clearly visible.

Iron is estimated volumetrically in a separate portion.

C. H. D.

Estimation of Manganese in Iron and Steel according to the Bismuth Method. H. KINDER [*Chemikerkommission des Vereins deutscher Eisenhüttenleute*] (*Stahl u. Eisen*, **37**, 197—202; from *Chem. Zentr.*, 1917, i, 817—818).—In continuation of previous work on the estimation of manganese by the permanganate (*Stahl u. Eisen*, 1913, **33**, 633) and chlorate or persulphate (*ibid.*, 1915, **35**, 918) methods, the commission has examined the data concerning the bismuth process, using sodium bismuthate or bismuth tetroxide. The original memoir must be consulted for details. The method, however, is not suited for purposes of investigation, and cannot be recommended for the works laboratory because of its complicated nature and the necessity of keeping the temperature below 25° (increase of temperature causes low results for Mn). The Volhard-Wolff permanganate method is suitable for

investigation, and can be used in the examination of ores, raw iron, steel, and ferromanganese. It can be employed equally well in hydrochloric or nitric acid solution, but sulphuric acid solutions are to be avoided. The presence of chromium is immaterial if the precipitated zinc oxide is removed; molybdenum and vanadium are without influence, but cobalt, which is usually only present in small amount, causes high results. The chlorate process can only be employed in nitric acid solution, and is particularly suitable for iron and steel; it is less accurate for estimating small amounts of manganese and for ferromanganese. Considerable quantities of chromium cause slightly high results. The persulphate process is adapted to works practice because of its rapidity. The presence of considerable quantities of chromium or cobalt makes the end-point difficult to detect on account of the yellow or pink colorations which they impart to the solutions.

H. W.

Evaluation of Pyrolusite. E. RUPP (*Arch. Pharm.*, 1916, **254**, 135—137).—To 0·2 gram of very finely powdered pyrolusite are added 3 grams of potassium iodide, 3 grams of sodium phosphate, 10 c.c. of water, and 10 c.c. of officinal (25%) phosphoric acid. The mixture is well shaken for one minute, and kept for thirty to sixty minutes with occasional shaking; about 50 c.c. of water are then added, and the liberated iodine is titrated with *N*/10-thiosulphate with starch as indicator. A reappearance of the blue coloration indicates that the pyrolusite has not been sufficiently finely ground.

C. S.

Differential Iodometry. IV. The Analysis of Pyrolusite and other Oxidised Manganese Ores. O. L. BARNEBEY and GEO. M. BISHOP (*J. Amer. Chem. Soc.*, 1917, **39**, 1235—1238. Compare this vol., ii, 274).—In a previous paper a method was described for the estimation of the available oxygen in pyrolusite and other higher oxides of manganese (*loc. cit.*). This method, however, is untrustworthy if appreciable amounts of ferric iron are present. The present paper gives an account of a method which may be used for pyrolusite containing large amounts of iron. The method depends on two principles: (1) When finely divided pyrolusite is treated with hydrochloric acid and potassium iodide, iodine is liberated; iodine is also liberated by ferric chloride in acid solution. (2) When neutral ferrous chloride is brought into contact with excess of iodine, it is instantaneously oxidised to the ferric condition. The following is the method recommended. A sample of the finely powdered ore (0·2 gram) is placed in a 300 c.c. flask and treated with 10 c.c. of *N*-sodium iodide and 5 c.c. of concentrated hydrochloric acid. The flask is repeatedly shaken until the reaction is complete; 0·2—0·5 gram of powdered sodium tartrate is then added, and the solution diluted to 150 c.c. Sodium hydrogen carbonate is added in excess and the free iodine titrated with arsenite. The addition of tartrate

is to prevent hydrolysis of the ferric salts on dilution. The results agree well with those obtained by other methods. J. F. S.

Iron Oxide as Standard in the Volumetric Estimation of Iron in Hydrochloric Acid Solution. H. KINDER (*Stahl u. Eisen*, **37**, 266; from *Chem. Zentr.*, 1917, i, 817).—A discussion of the proposal of Brandt (A., 1916, ii, 539) to use pure iron oxide, prepared from ferrous oxalate, as standard. H. W.

Ammonio-cobalt Molybdate, Tungstate, and Vanadate. Estimation and Separation of Cobalt. ADOLPHE CARNOT (*Compt. rend.*, 1917, **164**, 897—903.* Compare A., 1889, 1116, 1117).—The cobaltous chloride is converted into roseo- or purpureo-cobalt chloride by means of hydrogen peroxide in the presence of ammonium chloride and ammonia, and the solution is just neutralised with hydrochloric or acetic acids. To the cold, dilute solution just sufficient of a 5% aqueous solution of ammonium molybdate is added. The pink precipitate is dried at 110° and weighed. It has the composition $Co_2O_3,10NH_3,6MoO_3$. If this precipitate is ignited, the ammonia is driven off, and at the same time the cobalt sesquioxide and the molybdic anhydride are partly reduced. If ammonium tungstate is used instead of the molybdate, the precipitate obtained, when dried at 110°, has the composition $Co_2O_3,10NH_3,6WO_3,xH_2O$. With ammonium vanadate a pink precipitate is first obtained having the composition $Co_2O_3,10NH_3,3V_2O_5$, but with an excess of the vanadate solution a yellow precipitate is obtained having the composition $Co_2O_3,10NH_3,6V_2O_5$. It is most satisfactory for quantitative work to weigh the cobalt as the double molybdate. This method can be used for the estimation of cobalt in the presence of nickel, provided that the estimation is carried out rapidly and the precipitate is well washed with water. If the nickel is in excess, it is advisable to redissolve the precipitate in ammonia and reprecipitate it by neutralisation with acid and the addition of a little ammonium molybdate. Any iron and manganese present in the original solution will be precipitated by the ammonium hydroxide and hydrogen peroxide. In the presence of zinc, cadmium, or copper, it is advisable to dissolve and reprecipitate the double molybdate twice. W. G.

α-Benzildioxime [Reagent for Nickel]. HERMANN GROSSMANN and JULIE MANNHEIM (*Ber.*, 1917, **50**, 708—711).—The authors have tested Atack's method for detecting and estimating nickel in which α-benzildioxime is the precipitant (A., 1913, ii, 730). The reagent is best prepared by warming a methyl-alcoholic solution of benzil with powdered hydroxylamine hydrochloride and a few drops of hydrochloric acid, the oxime being filtered off from time to time. It is applied in the form of a saturated, alcoholic solution. For the separation of nickel from zinc or magnesium, ammonium chloride is added; manganese is retained in solution by means of citric acid and hydrazine (to prevent oxidation);

* and *Ann. Chim. anal.*, 1917, **22**, 121—126.

copper is kept in solution by means of Rochelle salt, but only small proportions should be present. The nickel precipitate does not suffer loss of weight even at 180°. J. C. W.

Analysis of Cast Nichrome. E. W. REID (*J. Ind. Eng. Chem.*, 1917, **9**, 488—490).—A detailed description is given of a scheme for the complete analysis of nickel–iron–chromium alloys. The alloy is first dissolved in nitrohydrochloric acid, and the silicon volatilised from the residue by treatment with hydrofluoric acid. The small residue of metal initially enclosed by the silica is now dissolved by a second treatment with nitrohydrochloric acid after fusion, if necessary, with sodium peroxide. In fractions of the 'stock' solution of the alloy thus obtained, the metals are estimated in the order given: (*a*) nickel by the cyanide method; (*b*) iron and chromium by precipitation as hydroxides and oxidation to ferric hydroxide and chromate respectively with bromine water; (*c*) manganese by precipitation with potassium chlorate in presence of nitric acid and titration of the precipitate with ferrous ammonium sulphate, zinc in the filtrate from the iron and chromium estimation after removal of the nickel by means of dimethylglyoxime, by titration with potassium ferrocyanide, and, finally, carbon by direct combustion in oxygen. G. F. M.

Estimation of Chromium in Ferrochrome. P. KOCH (*Stahl u. Eisen*, **37**, 266; from *Chem. Zentr.*, 1917, i, 817. Compare this vol., ii, 337).—In contrast to Schumacher (this vol., ii, 337), the author maintains the correctness of the factor 0·3109 by which the iron titre must be multiplied to obtain the chromium titre.
H. W.

Separation of Antimony and Tin by Hydrogen Sulphide in Hydrochloric Acid Solution, and their Iodometric Estimation. AUG. PRIM (*Chem. Zeit.*, 1917, **41**, 414—415).—Antimony and tin (stannous) can be completely separated by means of hydrogen sulphide if the solution contains a certain amount of hydrochloric acid. Preliminary tests with pure materials show that the best conditions are when the volume of liquid is 200 c.c. and the amount of hydrogen chloride present 26·58 grams (60 c.c. of acid of D 1·19). The antimony sulphide may be dissolved in concentrated hydrochloric acid and estimated iodometrically in the usual way after boiling away the hydrogen sulphide. The filtrate containing stannous chloride may also be boiled to remove hydrogen sulphide, with the addition of ferrum reductum, and finally titrated with iodine.

The application of the process to the analysis of alloys will be described later. J. C. W.

Detection of Methyl Alcohol by Catalytic Dehydrogenation. C. MANNICH and W. GEILMANN (*Arch. Pharm.*, 1916, **254**, 50—64).—The method consists in passing the vapour of the liquid under examination over pumice impregnated with reduced copper at 280—300°. The course of the decomposition has been already

described (A., 1916, i, 362). The formaldehyde produced is detected by the violet coloration it develops with morphine and concentrated sulphuric acid. The apparatus is figured and described. An aqueous solution containing 0·1% of methyl alcohol gives a condensate which develops the coloration very faintly after one hour and faintly after twenty-four hours. The method is very effective in detecting methyl alcohol in blood or urine, 0·01 gram of the alcohol in 100 c.c. of blood or urine giving a positive result; the liquid must first be carefully fractionated to concentrate the methyl alcohol, and the fraction containing the latter must be boiled for some time with freshly ignited animal charcoal before being passed over the catalyst, although even with these precautions the catalyst is slowly poisoned.

In order to detect methyl alcohol in the presence of ethyl alcohol, the mixture, diluted if necessary so that it contains about 50% of water, is passed over the catalyst, the condensate is heated in a vacuum to remove the acetaldehyde, and the residual solution is tested for formaldehyde as above. If the original mixture contains less than 1% of methyl alcohol, the diluted solution should be repeatedly fractionated before the test is applied to the fraction in which the methyl alcohol has been concentrated. One-half per cent. of methyl alcohol in brandy can be detected by this method. C. S.

Estimation of Alcohol and Water in Ether for Anæsthesia. R. L. Perkins (*J. Ind. Eng. Chem.*, 1917, **9**, 521—523).—The method differs from that of Mallinckrodt and Alt (A., 1916, ii, 583) in that the water is estimated from the specific gravity of the original mixture, and for this purpose specific gravities of ether–alcohol–water mixtures were determined to the fifth place of decimals, and the results are presented in the form of a curve, specific gravities being plotted against percentages of alcohol for varying proportions of water up to 1%. The specific gravities of the original ether and of the sample after drying for twenty-four hours over potassium carbonate are determined at 25°, and percentages of alcohol and water can then be read off directly from the above-mentioned curve. G. F. M.

Solubility of Cholesterol-digitonide. J. Howard Mueller (*J. Biol. Chem.*, 1917, **30**, 39—40. Compare Bloor and Knudson, A., 1916, ii, 650).—Bloor contends that the low figures obtained in the estimation of cholesterol by gravimetric as compared with colorimetric methods are due to losses incurred in the washing of the cholesterol–digitonide with ether and hot water. The author finds, however, that the solubility of the pure digitonide in either of these solvents is so slight that any error arising from this cause would not account for more than 10% of the discrepancy actually observed. H. W. B.

Estimation of Dextrose in Urine. G. Frerichs and E. Mannheim (*Arch. Pharm.*, 1916, **254**, 138—148).—The authors prefer Rupp and Lehmann's iodometric method of estimating

reducing sugars to the Fehling-Soxhlet method, and deny Ruoss's statement (A., 1916, ii, 155) that the iodometric estimation of the excess of the cupric salt remaining after Fehling's solution has been partly reduced by a sugar solution yields untrustworthy results, owing to the action of oxidised sugar compounds on the liberated iodine. They find that the substances produced from the sugar by the action of the alkaline copper solution have no action on iodine. The table published by Rupp and Lehmann giving the number of mg. of dextrose corresponding with a given consumption of *N*/10-thiosulphate has been incorrectly calculated, and the authors give a list of corrected values.

In estimating the sugar in urine, Rupp and Lehmann add 20 c.c. of the urine, diluted if necessary so that not more than 0·5% of dextrose is present, to a definite quantity of the Fehling's solution under definite conditions. In preference to this, the authors adopt the following quantities, since the use of tables is thereby avoided and the calculation of the result is greatly simplified. They have observed from the figures given in the table that when the number of mg. of dextrose is divided by the number of c.c. of *N*/10-thiosulphate, the quotients vary from 3·23 to 3·42. Taking the mean value (1 c.c. of *N*/10-thiosulphate is equivalent to 3·33 mg. of dextrose), the error in the calculation is in the most unfavourable cases only about one-thirtieth of the amount of sugar present. The authors therefore use for the estimation 3·33 c.c. of urine (readily measured by diluting 10 c.c. of the urine with 20 c.c. of water and taking 10 c.c. of the mixture) and 15 c.c. of the copper sulphate solution (70 grams of hydrated copper sulphate dissolved and made up to 1 litre); with these quantities, the percentage amount of dextrose (that is, the mg. of dextrose in 100 c.c. of urine) is almost exactly equal to one-tenth of the number of c.c. of *N*/10-thiosulphate representing the difference between the volume of thiosulphate required in standardising 15 c.c. of the copper sulphate solution and that used in titrating the excess of copper sulphate in the estimation. When the urine contains less than 1% of dextrose, 10 c.c. of undiluted urine should be used, and for less than 0·5% of dextrose 20 c.c. of undiluted urine, the percentage of dextrose being then obtained by dividing the above difference by 30 and by 60 respectively. When more than 3·5% of dextrose is present, one-half of 3·33 c.c. of urine should be used, the above difference being multiplied by 5 to give the percentage of dextrose.

The original should be consulted for a detailed description of the method of procedure. When 10 or 20 c.c. of undiluted urine are used, the iodine value (in c.c. of *N*/10-iodine) of this quantity must be estimated and subtracted from the difference mentioned above. C. S.

Estimation of Small Amounts of Sugar in the Urine. ALMA HILLER (*J. Biol. Chem.*, 1917, **30**, 125—127).—In this method, the creatinine and reducing substances other than dextrose are first removed from the urine by treatment with animal char-

coal and picric acid (Folin, A., 1915, ii, 802), and the dextrose in the filtrate is then estimated by Lewis and Benedict's method (A., 1915, ii, 111). H. W. B.

A New Method for the Estimation of Aldoses. J. Bougault (*Compt. rend.*, 1917, **164**, 1008—1011).—The method is based on the reaction $R{\cdot}CHO + H_2O + 2I = R{\cdot}CO_2H + 2HI$, which is, however, not instantaneous, the velocity depending on the excess of iodine used. The sugar, in aqueous solution, is heated with about three times the theoretical amount of iodine and a 15% solution of crystalline sodium carbonate. The oxidation is complete at the end of thirty minutes, after which the excess of iodine is titrated with sodium hyposulphite solution. The method was found to be applicable to all the aldoses tried, except that in the case of mannose the mixture had to be boiled for ninety minutes. The author has studied the action of iodine and sodium carbonate on the ketoses and the non-reducing sugars, and the influence of alkalinity, temperature, and light on the velocity of oxidation, and the estimation of aldoses in the presence of ketoses and non-reducing sugars. In all cases there is a slight secondary reaction, which can be allowed for by determining the amount of iodine absorbed during a further thirty minutes' heating. The ketoses and the non-reducing sugars are not appreciably oxidised by the reagent, and thus do not interfere with the estimation of aldoses unless they are present in excessive amounts.
W. G.

Simplified Inversion Process for the Estimation of Sucrose by Double Polarisation. Herbert S. Walker (*J. Ind. Eng. Chem.*, 1917, **9**, 490—492).—Certain of the difficulties encountered in the inversion of sucrose in the Herzfeld-Clerget method of estimation by double polarisation are obviated by the following method of procedure, which is specially recommended for technical practice. The solution used for direct polarisation is placed in a 100 c.c. flask and heated on a water-bath at 65—67°; it is then removed from the bath, 10 c.c. of diluted hydrochloric acid (1:1) are added, and the whole allowed to cool spontaneously in air. After fifteen minutes inversion is complete, and the solution, made up to 100 c.c., is ready for polarisation. In the case of products which have been clarified with basic lead acetate, the excess alkalinity must be destroyed before heating on the water-bath by adding 1 to 2 c.c. of the above diluted hydrochloric acid, otherwise serious losses occur. Errors due to destruction of lævulose are by this method of inversion largely eliminated, and the rigid adherence to specified temperatures and duration of heating required by the Herzfeld method is unnecessary, a latitude of 10° in temperature causing no appreciable inaccuracy in results. G. F. M.

Biological Examination of Honey. J. Gadamer [with Karl Laske] (*Arch. Pharm.*, 1916, **254**, 306—345).—One of the most

difficult tasks of the food analyst is to prove the genuineness of bee-honey by chemical analysis, especially since solutions of very pure invert-sugar with or without raffinose, which can be used to adulterate natural honey or to prepare artificial honey, have become easily obtainable. Fiehe's reaction, which detects hydroxymethylfurfuraldehyde in technical invert-sugar, is not conclusive, and methods based on the estimation of the nitrogen and albumin in natural honey are easily evaded.

The precipitin reactions of Kraus (A., 1904, ii, 423), Wassermann, and Uhlenhuth could be usefully employed in the examination of honey provided the proteins occurring in the honey originate in the bee's body and not in the plant from the nectaries of which the bee collects the material of which the honey is made. In 1902 von Rigler prepared an anti-serum specific for genuine honey, and in the same year Langer obtained a serum which gave a copious precipitate with buck-wheat honey. The researches of the latter investigator show that the honey albumin is quite independent of the plant visited by the bee.

An important advance was made by Thöni (*Veroffl. Schweiz. Ges.-amt*, 1911, **2**, 80; 1912, **3**, 74), who placed the precipitin method on a more or less quantitative basis and ascertained the amount of precipitate normally given by a genuine unheated bee-honey under definite experimental conditions. Since Klostermann (*Jahrsb. Hyg. Inst. Halle*, 1909) has reported less favourably on the precipitin method, the authors have reinvestigated the subject. In order to obtain the antigens, a sample of genuine honey (75 grams) was dialysed for forty-eight hours, the sugar-free liquid was shaken with 70% of finely powdered ammonium sulphate, the albumins were collected after two hours, suspended in 10 grams of sterilised, distilled water, and, after the addition of 0·5% of toluene, dialysed for about forty-eight hours to remove the ammonium sulphate. Each dialysis yielded about 20 grams of injection liquid. To obtain the anti-substance, as a preliminary the normal serum of each dog was tested with 2—10% solutions of the honey used to supply the antigens; in no case was a precipitate obtained after five hours. The albumin suspensions, freshly prepared in every case, were introduced (3—6 c.c.) by intraperitoneal injection for several weeks at intervals of a few days, eight to twelve injections being made. Samples of blood were withdrawn at intervals and the anti-sera obtained tested, after filtration through kieselguhr, for their activity and specificity. Suitable anti-sera (0·2—0·5 c.c.) were mixed with 1 c.c. of 1—10% honey solutions, of 10% artificial honey solution, of 10% starch syrup solution, also 0·5 c.c. of normal serum was mixed with 1 c.c. of 10% honey solution; each mixture, after the addition of one drop of toluene, was vigorously shaken and kept at 37° for five hours, the tubes were centrifuged (1500 rev. per minute) for five minutes, and the volume of the precipitate (if any) read off in mm.

The authors have set themselves the questions: (1) does the preservative toluene affect the reaction and is its addition neces-

sary; (2) is the precipitation constantly quantitative, in other words, do two different anti-sera, which yield equal amounts of precipitates with one honey, also give equal amounts with another honey; (3) are the precipitates obtained from 10%, 2%, and 1% honey solutions quantitatively comparable; and (4) does the storing of honey effect any change in its content of specific albumins? They find that: (1) Preservation of the liquid during the time of the experiment is unnecessary. The presence of toluene causes the formation of emulsions and renders a quantitative separation of the precipitate by centrifuging impossible. In the absence of toluene, quantitative results are obtained. (2) An absolute constancy in the activity of the precipitating serum cannot be claimed. Different anti-sera give approximately equal amounts of precipitate, but the variations are not so great as to render the method inapplicable for quantitative purposes. (3) With a given anti-serum, the amounts of precipitate obtained from 2% and 1% solutions of a honey are by no means comparable; therefore, in examining a honey by the biological method, only the values obtained with a 10% solution should be utilised. (4) The amount of precipitate obtained from a given honey and the same anti-serum is the same during the period of one year. A specimen of genuine honey which had been kept for eleven years gave, however, only a very small precipitate.

The authors are of opinion, therefore, that the precipitin reaction has a real quantitative value. All honeys which do not give a precipitate with honey albumin anti-serum are not to be regarded as genuine bee-honeys. If a precipitate is obtained and its amount corresponds with that obtained from the control honey, the honey under examination is genuine. If the amount of the precipitate is smaller than that given by the control, the honey under examination is either genuine honey which has been heated or honey which has been adulterated.

The paper contains numerous tables of results and concludes with a bibliography of the subject. C. S.

Examination of Acetic Anhydride. L. G. RADCLIFFE and F. MEDOFSKI (*J. Soc. Chem. Ind.*, 1917, **36**, 628—630).—The authors have examined various methods of estimating acetic anhydride in the commercial product, and are led to the conclusion that the direct titration process (decomposition of anhydride by water and estimation of the acid by titration with $N/1$-sodium hydroxide) is the shortest, but the British Expert Committee's method (Report on the Analysis of Crude Glycerine, 1911) is the safest, since the results derived from direct titration are controlled by the data obtained by allowing weighed quantities of the anhydride to react with a considerable excess of aniline and estimating the acid formed.

Much of the acetic anhydride now available is yellow, and the coloration is difficult to remove by simple distillation; it may be eliminated by distillation over phosphoric anhydride, but the

process causes a slight diminution in the content of acetic anhydride.

According to the authors' experience, crystalline sodium acetate does not effloresce on exposure to air, but can be readily completely dehydrated at 97—100° or by the aid of calcium chloride at the ordinary temperature. The anhydrous substance is very hygroscopic. H. W.

Testing of Acetic Anhydride. C. E. SAGE (*Perfumery and Ess. Oil Rec.*, 1917, **8**, 162—163; from *J. Soc. Chem. Ind.*, 1917, **36**, 667—668).—In estimating the value of acetic anhydride, the total acidity is determined by direct titration with alkali hydroxide solution and also the residual acidity after treatment with aniline in the cold, by which the anhydride is decomposed with the production of equimolecular parts of acetanilide and acetic acid. From these two titration numbers, the amount of anhydride is calculated, the remaining acidity being due to acetic acid or to acetic and butyric acids if the latter is present, which is determined by a preliminary qualitative analysis; the relative proportions of these two acids may also be calculated from the same titrations. It is suggested from the figures obtained and the large-scale results when using anhydride containing butyric acid that anhydrides other than acetic may also be present. H. W.

Shaffer's Oxidation Method for the Estimation of β-Hydroxybutyric Acid in Urine. N. O. ENGFELDT (*Zeitsch. physiol. Chem.*, 1917, **99**, 166—223).—The author finds that although the oxidation of β-hydroxybutyric acid to acetone by chromic acid is not quantitative, yet Shaffer's method for the estimation of β-hydroxybutyric acid in urine by this means yields satisfactory results provided certain precautions are taken and corrections applied. H. W. B.

Improvements in the Copper Method for Estimating Amino-acids. PHILIP ADOLPH KOBER (*J. Ind. Eng. Chem.*, 1917, **9**, 501—504).—Certain improvements are described in the technique of the copper method for estimating amino-acids. As an easily prepared iodometric standard, a copper sulphate solution prepared from anhydrous copper sulphate is recommended, and a simple method for its preparation by dehydrating the salt in a test-tube heated in an oil-bath at 250° is described. A stock suspension of cupric hydroxide, which retains its activity for months and obviates the necessity of a fresh preparation every day, is obtained by precipitating with less alkali than is required for the complete precipitation of the copper. To avoid the daily preparation of potassium iodide starch solutions, a saturated solution may be prepared and kept almost indefinitely in a flask under a layer of oil after boiling for thirty minutes to expel oxygen, the neck of the flask being closed with a bung carrying a trap containing strong sodium hydroxide. In conclusion, a summarised description of the complete amino-acid estimation is given.

G. F. M.

Simple Method of Estimating the Contents of Sozoiodol-mercury Preparations. A. HERRMANN (*Arch. Pharm.*, 1916, **254**, 498—500. Compare Rupp and Hermann, this vol., i, 488). —The mercury in hydrargyrum sozoiodolicum (mercuric salt of di-iodophenol-*p*-sulphonic acid, $C_6H_2I_2<\begin{smallmatrix}O-\\SO_3\end{smallmatrix}>Hg$) is readily estimated as follows. The preparation, 0·5 gram, is shaken with about 10 c.c. of water in a 200-gram glass-stoppered bottle, treated with 2 grams of potassium iodide, and, after the liberated mercuric iodide has dissolved, basified with 10 c.c. of officinal alkali hydroxide solution. A mixture of 3 c.c. of formaldehyde solution and about 10 c.c. of water is added, and the bottle is gently shaken for about one minute. After acidifying with 25 c.c. of dilute acetic acid, 25 c.c. of *N*/10-iodine solution are added, and the excess of the iodine is titrated with *N*/10-thiosulphate after all the mercury has been dissolved (1 c.c. of *N*/10-iodine = 0·01003 gram of mercury = 0·031225 gram of the mercuric salt).

The mercury in anogon (the mercurous salt, $OHg\cdot C_6H_2I_2\cdot SO_3Hg$) is estimated by treating 0·5 gram with 2 grams of potassium iodide and 25 c.c. of *N*/10-iodine, shaking the mixture for one to three minutes, and titrating the excess of iodine with *N*/10-thiosulphate and starch solution (1 c.c. of *N*/10-iodine = 0·02006 gram of mercury = 0·041256 gram of the mercurous salt). C. S.

The Examination of Oils used in Soap-making. RAOUL LECOQ (*Bull. Soc. chim.*, 1917, [iv], **21**, 101—103).—A brief account of a general method stated to be capable of giving good results with all oils. A small quantity of soap is prepared from the oil by alcoholic saponification. Ten grams of this are dissolved in 50 c.c. of water and emulsified with 100 grams of the oil. The mixture is heated on a water-bath, and to it is added, in five successive portions at half-hour intervals, the calculated quantity of sodium hydroxide dissolved in 60 c.c. of water. The mixture is heated for one and a-half hours. The soap is separated, dissolved in 400 c.c. of water, and precipitated by the addition of 125 grams of salt. The soap thus obtained is decanted and washed at the pump, and when cold is examined. W. G.

Estimation of Acetone Substances in the Urine. EMIL LENK (*Biochem. Zeitsch.*, 1916, **78**, 224—230).—The method employed was an iodometric one, in which the substances acting on iodine were first destroyed by treatment with permanganate, and the acetone substances were then directly estimated in the urine without distillation. It was found that the preformed acetone could be estimated by heating the urine with permanganate and acetic acid, in which case the acetoacetic acid is not converted into acetone. After destruction of excess of permanganate with oxalic acid, and precipitation of the manganese hydroxide with sodium hydroxide, the iodometric estimation is carried out in the usual way. To estimate the combined acetone and acetoacetic acid, the urine is first heated with oxalic acid, by means

of which the acetoacetic acid is converted into acetone. The total acetone is then estimated by the method above described (boiling with permanganate in solution acidified by acetic acid, etc.). Accurate results can be obtained when only 1 c.c. of urine is employed for the analysis. S. B. S.

Evaluation of Podophyllin. HEINRICH TANZEN (*Arch. Pharm.*, 1916, **254**, 44—49).—The paper gives an account of the extraction of podophyllin from the rhizomes of *Podophyllum peltatum*, Linné, and of the properties of its known constituents, makes a brief comparison between the American and the Indian varieties, and discusses the methods of Jenkins, Gordin and Merrel, Umney, Kremel, and the Dutch pharmacopœia for the estimation of the podophyllotoxin contained therein. The first three methods are condemned on account of the large amount of material required. The last method is recommended. C. S.

Iodine as a Useful Microchemical Reagent for Tannin, especially as regards the Distribution of Tannin and Starch in Vegetable Tissues. ADOLF SPERLICH (*Ber. Deut. bot. Ges.*, 1917, **35**, 69—73).—Iodine in traces may penetrate into cells without injury to the living plasma, the tannins dissolved in the cell-sap gradually forming resistant, characteristic substances of different shades of brown. The substances formed are probably oxidation products allied to or identical with phlobaphens. Other substances, such as oils, resins, etc., also fix iodine, which is removable more or less easily and rapidly by alcohol of various concentrations. The compounds formed in the above way by tannins are highly stable, and the sections may be subjected to further staining operations. T. H. P.

Colorimetric Estimation of Serum-Albumin and Globulin in Urine, Ascitic Fluid, and Blood Serum. W. AUTENRIETH (*Munch. med. Woch.*, 1917, **64**, 241—245; from *Chem. Zentr.*, 1917, i, 699. Compare A., 1916, ii, 163).—The two proteins are estimated together, the method being based on the biuret reaction; the colorations obtained are observed in the Autenrieth–Koenigsberger colorimeter, which is provided with a special "albumin" scale. W. P. S.

Micro-titration with Formaldehyde and its Applications in Physiology. III. Detection of Arginase. A. CLEMENTI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 261—264).—Micro-titration with formaldehyde (A., 1915, i, 1025) may be applied to the author's titrimetric method for the investigation of arginase (A., 1915, i, 912), 0·5 c.c. of an arginine sulphate solution containing 0·8% of the base being sufficient to show the action of the enzyme. Arginase is found in the liver of the human embryo, but not in that of the reptile, *Zamenensis Viridiflavus*. T. H. P.

General and Physical Chemistry.

The Distinction between Methylated Nitroanilines and their Nitrosoamines by means of Refractometric Determinations. J. D. JANSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1098—1100).—The following molecular refractivities are recorded: 3:4-dinitrodimethylaniline, 62·8; 3:6-dinitrodimethylaniline, 56·8; 3:4-dinitrodiethylaniline, 73·1; 3:6-dinitrodiethylaniline, 65·3; 3:4-dinitrophenylmethylnitrosoamine, 55·2; 3:6-dinitrophenylmethylnitrosoamine, 52·8; 3 : 4-dinitrophenylethylnitrosoamine, 59·6; 3:6-dinitrophenylethylnitrosoamine, 57·2.

The difference between the molecular refractivities of the isomeric nitrosoamines is much smaller than that for the corresponding dialkyl compounds. It is also pointed out that the specific refractions of the dinitrodialkylanilines are much greater than the corresponding values for the nitrosoamines. It is suggested that this may be conveniently utilised as a means of distinguishing between the two groups of substances. H. M. D.

The Effect of an Electric Field on the Spectrum Lines of Hydrogen. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 137—146).—The method of Lo Surdo (*Atti R. Accad. Lincei*, 1913, [v], **22**, 664) has been employed in the further investigation of the influence of an electric field on the hydrogen lines. In this method the spectrum of the glow in the region of discharge immediately in front of the cathode is submitted to investigation, the potential gradient in this region being very large.

The most satisfactory results were obtained with the H_γ line, for which, in addition to the two outer parallel and three perpendicular components, the authors' photographs reveal the existence of four inner parallel components and two inner perpendicular components. These have been identified with components which Stark's method of observation has already shown to occur in the electrically resolved spectrum.

The separation of the inner component lines is found to be proportional to the intensity of the electric field. H. M. D.

The Triplet Series of Radium. GLADYS A. ANSLOW and JANET T. HOWELL (*Proc. Nat. Acad. Sci.*, 1917, **3**, 409—412).—The elements of the second group of the periodic table are characterised by the fact that the principal, first, and second subordinate series of spectral lines contain doublet and triplet series. If the logarithms of the frequency differences between the extreme members of the triplets are plotted against the logarithms of the atomic numbers of the corresponding elements, it is found that alternate elements fall on straight lines. The straight line passing through calcium, strontium, barium, and radium indicates

that the frequency difference for the radium triplets should be approximately 3060.

The known radium lines give triplets with average frequency differences of 2016·64, 1036·15, and 3052·79, and it would seem that the last frequency difference is characteristic of the radium spectrum. The first line of the triplet combinations in the principal series is given by $m = 44349{\cdot}0 - 109675/(m + 1{\cdot}0855)^2$, in the first subordinate series by $m = 25236{\cdot}8 - 109675/(m + 0{\cdot}8062)^2$, and in the second subordinate series by $m = 25153{\cdot}0 - 109675/(m + 0{\cdot}6196)^2$. H. M. D.

Spectra of High Frequency. MANNE SIEGBAHN (*Compt. rend.*, 1917, **165**, 59. Compare A., 1916, ii, 362, 405).—A claim for priority over Ledoux-Lebard and Dauvillier (this vol., ii, 283). W. G.

The Spark and the Vacuum Arc Spectra of some Metals in the Extreme Ultra-violet. TOSHIO TAKAMINE and SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 117—135).—The wave-lengths of lines in the spark spectra of silver, aluminium, gold, bismuth, cadmium, cobalt, iron, manganese, platinum, antimony, and thallium have been measured over the region λ 2000—λ 1830 by using a quartz spectrograph and Schumann plates. In every case, new lines were observed in the most refrangible portion of the ultra-violet region.

The vacuum arc spectra of bismuth, antimony, and thallium were also photographed and several new lines detected for each element in the region λ 2000—λ 1850. H. M. D.

The Occurrence of Harmonics in the Infra-red Absorption Spectra of Diatomic Gases. JAMES B. BRINSMADE and EDWIN C. KEMBLE (*Proc. Nat. Acad. Sci.*, 1917, **3**, 420—425).—With reference to Bjerrum's explanation of the structure of the infra-red absorption bands of gases, an examination has been made of the infra-red spectra of hydrogen chloride and hydrogen bromide. In accordance with the requirements of the quantum hypothesis, first harmonics have been found in the spectra of both gases. The structure of these bands, as well as that of the corresponding weak carbon monoxide band, is found to be in general agreement with theory. Although an attempt was made to detect second and third harmonics in the spectra of hydrogen chloride and carbon monoxide, these experiments gave a negative result. H. M. D.

Qualitative Spectrum Analysis of Organic Dyestuffs by Formánek's Method. JOS. POKORNÝ (*J. Soc. Dyers*, 1917, **33**, 162—166).—A reply to criticisms of the mode of interpreting the spectral observations in Formánek's method of detecting organic dyes. H. M. D.

Inquiries into the Explanation of Radium Disintegration. TARINI CHARAN CHOUDHARI (*Chem. News*, 1917, **116**, 25—27).—The paper discusses the origin of the excess of hydrogen in the

radioactive decomposition of water, the loss of weight of a radium salt by disintegration, and the fate of the halogen in radium haloid when the radium disintegrates, directing attention to the unexplained problems in connexion therewith. F. S.

"Spark-lengths" in various Gases and Vapours. Robert Wright (T., 1917, **111**, 643—649).—The variation of the length of the spark with the nature of the surrounding gas or vapour has been examined under conditions in which the form of the spark-gap, the temperature, pressure, and the voltage were the same for the different vapours experimented on. The voltage was maintained appreciably constant by arranging an air-gap of definite length in parallel with the vapour-gap, the length of the latter being adjusted so that sparking took place equally through the air- and vapour-gaps when the potential was carefully raised.

For series of chemically comparable substances the length of the vapour-gap decreases with increase in the molecular weight. In other words, the insulating power relative to that of air increases with the molecular weight of the substance. It should, however, be noted that the curves connecting potential and length of spark are not by any means parallel and may intersect one another. This intersection was actually observed in the case of carbon dioxide and air, the former being the better insulator at low potentials, whereas the reverse holds at higher potentials.

H. M. D.

Current Potentials of Electrolyte Solutions. II. H. R. Kruyt (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1021—1028. Compare A., 1914, ii, 837).—In the further investigation of the influence of electrolytes on the current potential, experiments have been made with solutions of hydrochloric acid and *p*-chloroaniline hydrochloride. In both cases the reduction of the current potential is much greater than that produced by potassium chloride. This result can be readily accounted for on the assumption that the phenomenon is dependent on the facility with which the respective cations are adsorbed.

According to Helmholtz's theory, the product of the current potential and the electrical conductivity of the flowing liquid affords a measure of the electric charge on the capillary tube. When the charge of the capillary obtained in this manner is plotted as a function of the concentration of the electrolyte, curves are obtained which show a maximum. In the case of potassium chloride, the maximum corresponds with a much larger concentration than that found for solutions of hydrochloric acid, barium chloride, and *p*-chloroaniline hydrochloride. These observations are obviously closely connected with those which have been made on the influence of electrolytes on the cataphoresis of oil emulsions, and attention is directed to the similarity between the results of these experiments. If the contact charges for the different electrolytes are compared at a concentration greater than those which correspond with the above-mentioned maxima, it is found that the order in which the electrolytes arrange themselves is the same as that which expresses

their relative coagulating powers. This again is in favour of the theory that the current potential is largely determined by ion absorption phenomena. H. M. D.

Hydrates of Alcohols and Fatty Acids. II. JOHANNE CHRISTIANSEN (*Zeitsch. physikal. Chem.*, 1917, **92**, 257—274. Compare A., 1916, ii, 75).—A continuation of the work previously published. Experiments are described which indicate that the position of the ballistic electric neutral point of aqueous solutions of alcohols and fatty acids is practically unaffected by change of temperature at low temperatures. It is shown that errors are introduced into the measurements by evaporation during the projection of solution on to the electrode, and as this evaporation is obviously dependent on the condition of the surrounding atmosphere experiments have been carried out in air (*a*) dried with calcium chloride, (*b*) saturated with the solution in question, (*c*) saturated with water vapour, (*d*) saturated with the alcohol or acid vapour, and (*e*) ordinary air. These experiments show that at 0° the errors introduced are unimportant. A series of determinations of the neutral point has therefore been made at 0° for solutions of methyl alcohol, ethyl alcohol, propyl alcohol, trimethylcarbinol, formic acid, acetic acid, propionic acid, and butyric acid in aqueous solutions containing definite quantities of sodium chloride. It is found that the ballistic electrically neutral solutions have compositions corresponding with definite hydrates. The following hydrates are therefore assumed to be present in the solutions: methyl alcohol, $1:2H_2O$; ethyl alcohol, $1:4H_2O$; propyl alcohol, $1:8H_2O$; trimethylcarbinol, $1:16H_2O$; acetic acid, $1:3H_2O$; propionic acid, $1:9H_2O$; and butyric acid, $1:27H_2O$. A theoretical interpretation of the connexion between the ballistic electric neutrality and the presence of a definite hydrate is given in the paper. J. F. S.

Electrolytic Migration. Electrolysis of Solutions of Mixed Alkaline Salts. MARC VAN LAER (*J. Chim. phys.*, 1917, **15**, 154—163).—The electrolysis of solutions of sodium carbonate has been examined from the point of view of current yield. It is shown that the resistance of the cell increases as the electrolysis proceeds owing to the formation and precipitation of sodium hydrogen carbonate. The addition of an oxy-salt of sodium to the carbonate decreases the formation of hydrogen carbonate and makes it possible to obtain directly cathode liquors which are very rich in sodium hydroxide. This addition (of nitrate or sulphate) also brings about a considerable increase in the current yield. The yield may be calculated by the formula of Foerster and Jorre, and since this is based on the transport numbers of the ions it follows directly that the results mentioned above are an immediate consequence of the ionic migration. The mechanism of the migration changes brought about by the addition of an oxy-salt is discussed in the paper. It is shown that by choice of a suitable diaphragm sodium carbonate may be directly and economically converted into sodium hydroxide by the electrolysis of aqueous solutions. J. F. S.

Ultra-microscopic Investigation of very thin Metal and Salt Films obtained by Evaporation in High Vacuum. W. REINDERS and L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 958—968).—The thin films deposited on the inside of the bulbs of incandescent lamps when various substances are heated to a sufficiently high temperature by the passage of the current through the metallic filament have been subjected to ultra-microscopic examination.

In the case of sodium chloride which has been deposited in these circumstances, the film appears to be optically homogeneous under the ultra-microscope, and it would seem that the sodium chloride is in an amorphous-vitreous condition comparable with that of an undercooled liquid. If the vacuous bulb is opened, so that moist air comes into contact with the film of salt, it quickly becomes opalescent, and the ultra-microscope reveals a network of ultramicrons. In course of time this network becomes distinctly coarser, and ultimately it is possible to recognise the presence of cubic micro-crystals. In dry air, the crystallisation process takes place very slowly, and the vitreous condition may be preserved if the layer of salt is covered by Canada balsam.

Metallic silver, when vaporised and condensed in the above manner yields a film the colour of which changes through greenish-yellow, orange, red, violet, and blue as the thickness increases. Under the ultra-microscope the red, violet, and blue films are distinctly heterogeneous, but the greenish-yellow film is apparently similar in structure to the sodium chloride deposit. Gold closely resembles silver in its behaviour, whilst tungsten only yields films of a grey or black colour, which could not be resolved under the ultra-microscope.

A comparison of the above with metal films obtained by cathode disintegration indicates that the latter consist as a rule of coarser particles than those which are present in the evaporation films.

H. M. D.

Relationship of Heat Capacity to Entropy. VLADIMIR NJEGOVAN (*Zeitsch. physikal. Chem.*, 1917, **92**, 275—286).—A mathematical paper in which it is shown that the heat capacity of a substance is proportional to the absolute value of the entropy. The following equations are developed. These express for gases the dependence of entropy (S) on temperature (T) and pressure (P) on the one hand, and on temperature and volume (v) on the other: $S = 2{\cdot}3026 C_p^T \log T - 4{\cdot}571 \log p_{at} + k$; $S = 2{\cdot}3026 C_v^T \log T + 4{\cdot}571 \log v_1 + w$.

J. F. S.

Critical Point, Critical Phenomena, and a few Condensation Constants of Air. J. P. KUENEN and A. L. CLARK (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1088—1098).—A detailed study has been made of the condensation phenomena in the critical region. According to the theory of mixtures, a distinction has to be made between the "plait point" at which the two coexisting phases become identical, and the "critical point of contact," which is the limiting condition for the separation into

two phases. The temperature and pressure corresponding with the "plait point" are $-140·73°$ and 37·25 atmospheres, and with the "critical point of contact" $-140·63°$ and 37·17 atmospheres. The density of the liquid at these points is 0·35 and 0·31. The critical density of air calculated from the critical densities of oxygen and nitrogen by the simple mixture rule is 0·34, which lies between the two values given above. H. M. D.

A Simple Exponential Function for the Representation of several Physico-chemical Phenomena. Vapour Tension of Liquids and Solids, Dissociation Pressure, Equilibrium Constants, Densities of Liquids and Vapours, and Radiation from Black Bodies. ALBERT SCHMIDT (*J. Chim. phys.*, 1917, **15**, 97—153).—A theoretical paper in which it is shown that the expression $\log p/p_1 = f_1 - k/\delta$ is more suited to the calculation of the vapour pressure of liquids and solids at different temperatures than the empirical formula of van der Waals. This expression contains two constants, k and δ, of which δ represents the temperature of origin, a temperature characteristic of the substance and different from the absolute zero, and k is a function of this temperature. A method is described by which these two constants may be graphically evaluated from known experimental data. Tables of the values of these constants are given for 114 liquid substances and 27 solid substances. The calculation of the vapour pressure of 14 substances, boiling between $-186°$ (argon) and $+925°$ (zinc), at various temperatures shows extremely well that the formula represents the change of pressure as a function of the temperature. The calculated values agree sufficiently well with the experimental values of different observers. This same formula has in twelve cases been applied to the calculation of the dissociation pressure at different temperatures. Tables of the calculated values are given along with the experimentally determined values; the agreement is particularly good. Some examples are given which show that this same relationship is equally applicable to the variations of the equilibrium constant of a gaseous system. Among other things, it is also shown that this formula represents the changes of the product of the liquid and gaseous densities of substances with change of temperature. The values of the constants have been calculated for 37 substances, and the value of the product has been calculated for chlorine and ether over a wide range of temperature. In both cases the results are in excellent agreement with the observed values of Young and Pellaton except at the higher temperatures, where considerable divergence is manifested. In these cases the calculation of the liquid density and the density of the saturated vapour shows that the combination of the present formula with the law of rectilinear diameters is capable of reproducing the changes of density of the two phases with temperature up to about 40° of the critical temperature. Finally, it is shown that this same formula is applicable to the radiation of absolutely black bodies at different temperatures. Tables are given showing the agreement between

(*a*) the luminous radiation and (*b*) the total radiation, with the observed values for temperatures between 100·1° and 1780°.

J. F. S.

Methods and Apparatus used in the Cryogenic Laboratory. XVII. Cryostat for Temperatures between 27° and 55° (absolute). H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1049—1058).—An apparatus is described which makes it possible to maintain constant temperatures over the range 27—55° absolute. This is attained by passing cooled gaseous hydrogen through liquid hydrogen contained in a specially constructed evaporator, the gas thus obtained, after being heated to the desired temperature, being conducted into the cryostat in which the experimental chamber is immersed. Experience has shown that the hydrogen vapour cryostat permits of the maintenance of temperatures for considerable intervals of time within the specified range with deviations which do not exceed 0·01°.

H. M. D.

Isothermals of Monatomic Substances and their Binary Mixtures. XVIII. A Preliminary Determination of the Critical Point of Neon. H. KAMERLINGH ONNES, C. A. CROMMELIN, and P. G. CATH (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1058—1062).—The construction of the thermostat described in the preceding abstract has enabled the authors to determine with accuracy the critical data for neon. The values found are: critical temperature, −228·35°; critical pressure, 26·86 atmos.

H. M. D.

A Method of Determining Molecular Weights. ÉDOUARD URBAIN (*Compt. rend.*, 1917, **165**, 65—67).—A mixture of two non-miscible, volatile liquids is distilled, and the distillate analysed. Using one liquid the constants of which are known, the vapour density of the second liquid is given by $d_1 = dpq_1/(H-p)q$, where d, p, and q are respectively the vapour density, pressure, and weight of the known liquid in 100 grams of distillate, d_1 and q_1 the corresponding constants for the liquid the molecular weight of which is being determined, and H the pressure under which the mixture is distilled. From the vapour density, the molecular weight of the liquid under examination can readily be calculated.

W. G.

The Additivity of the Specific Volume in Sols. H. R. KRUYT (*Kolloid Zeitsch.*, 1917, **20**, 239—242).—From measurements of the density of colloidal solutions, Wintgen (A., 1915, ii, 751) drew the conclusion that the volume relations in colloidal systems are exactly similar to those exhibited by true solutions. This conclusion is criticised, although it may be admitted that deviations from the mixture rule will be comparatively small in the case of colloidal solutions. H. M. D.

Measurement of Surface Tension by the Method of the Weight of Drops. F. LOUIS PERROT (*J. Chim. phys.*, 1917, **15**, 164—207, and *Arch. Sci. phys. nat.*, 1917, [iv], **43**, 476—486).—A review and criticism of the recent work on this subject, in which it is shown that the classic formula of the proportionality of the weight of a drop to its surface tension, $P=2\pi r\gamma$, ought to be definitely abandoned, since it is only a false approximation. The theory of Lohnstein, despite its static and capillary basis, may with advantage be tentatively allowed to replace the older formula. For physico-chemical investigations the method of Morgan, when subjected to the conditions and limitations placed on it by him, may be regarded as satisfactory. Up to the present no relationship between the weight of a falling drop and its other properties has been found. A bibliography of the literature of the subject from 1899 is appended to the paper. J. F. S.

Surface Tension and Cohesion in Metals and Alloys. SYDNEY W. SMITH (*J. Inst. Metals*, 1917, **17**, 65—118. Compare A., 1915, ii, 44).—The relations between surface tension and other physical properties of metals and alloys are discussed. Cases of liquation, as in the freezing of alloys of silver and copper, are explained by the considerable differences between the surface tensions and intrinsic pressures of the component metals. When the surface tensions and intrinsic pressures are practically equal, as in the alloys of gold and silver, or of silver and cadmium, liquation does not take place. The maximum hardness in a series of solid solutions usually occurs at a composition at which the products of the atomic percentages and the respective intrinsic pressures are equal. C. H. D.

The Viscosity of Liquefied Gases. VI. Observations on the Torsional Oscillatory Movement of a Sphere in a Viscous Liquid with Finite Angles of Deviation and Application of the Results obtained to the Determination of Viscosities. VII. The Torsional Oscillatory Motion of a Body of Revolution in a Viscous Liquid. VIII. The Similarity in the Oscillatory Rotation of a Body of Revolution in a Viscous Liquid. J. E. VERSCHAFFELT (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1062—1073, 1073—1079, 1079—1084).—A series of theoretical papers dealing with the oscillatory motion of a sphere or similar bodies of revolution in viscous media and the application of the method to the determination of the viscosities of fluids. H. M. D.

The Viscosity of Liquefied Gases. IX. Preliminary Determination of the Viscosity of Liquid Hydrogen. J. E. VERSCHAFFELT and CH. NICAISE (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1084—1088).—In consequence of the low value of the viscosity of liquid hydrogen, the damping of the oscillatory motion is very slight and the internal friction of the suspension wire is a factor of considerable importance in the determination. Ex-

periments showed that the internal friction at this low temperature varied within wide limits and was difficult to control. On this account the accuracy attainable is limited and the approximate value of the viscosity of liquid hydrogen at 20·36° abs. is given as 0·00011. The density of the liquid is 0·0708. H. M. D.

Fluidity. I. C. DRUCKER (*Zeitsch. physikal. Chem.*, 1917, **92**, 287—319).—A theoretical paper in which the following points are discussed at length: (*a*) viscosities of gases and gaseous mixtures; (*b*) viscosity and vapour pressure; (*c*) fluidity of liquid mixtures; and (*d*) fluidity and heat of fusion. Numerous curves and tables of results of other workers are introduced into the paper to illustrate the points raised in the discussion. It is shown that the viscosity of gases and liquids is closely related to surface phenomena; the effect of movement on the individual layers, and in particular on the layer adsorbed by the solid contact layer, can be referred to the dual influence of the viscosity-coefficient and the adsorptive-coefficient. The fluidity of liquid substances at different temperatures bears an almost linear relationship to the vapour pressure. The fluidity of binary liquid mixtures corresponds with a linear mixture formula, even when a chemical combination between the two liquids is present. In the latter case instead of a binary formula, a ternary or even a formula of a higher degree is necessary to represent the relationship. If, however, the complex or combined condition is sensitive to the volume change induced by movement, then a mixture formula can in no way represent the case. It is possible to calculate the heat change from the temperature-coefficient of the fluidity; this heat change is very close in value to the heat of fusion, and often is identical with it. The heat change of the spacial orientation of the crystals constitutes generally only a very small fraction of the heat of solidification.

J. F. S.

An Improved Bunsen Diffusion Apparatus. JEROME S. MARCUS (*J. Ind. Eng. Chem.*, 1917, **9**, 603).—A description of a modified all-glass apparatus designed to facilitate the introduction of the gas under investigation.

The gas is introduced by a three-way tap which later connects the diffusion tube with the aperture, the entry of the gas being regulated by running mercury from another three-way tap situated in the lowest part of the bend of the U-tube between the diffusion tube and the mercury reservoir. The reservoir is of considerable cross-section, and is filled to the same level for each experiment so as to give a constant initial head of mercury. D. F. T.

Studies of Solution. I. The Change of Molecular Solution Volumes in Solutions. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 1—43).—The method of Forch (A., 1903, ii, 714) has been used to calculate the molecular volumes of solute and solvent in aqueous solutions of sucrose, potassium chloride, sodium chloride, and ammonium chloride at temperatures ranging

from 0° to 50°. The curves obtained by plotting the molecular solution volume against the concentration show that the water contracts, the molecular volume of the solvent decreasing with increase in the concentration. Similarly, the curves for the solute show that this expands, the volume increasing with the concentration, although the rate of increase diminishes as the concentration increases.

The contraction of the solvent, which is brought about by admixture with the various solutes, is discussed with reference to the osmotic pressure of the solution and Tammann's internal pressure, and a modified method of calculating the internal pressure is described.

By reference to the molecular volumes of a large number of organic substances which are only sparingly soluble in water, it is shown that, in general, the solubility decreases with increase in the magnitude of the molecular volume. H. M. D.

Studies of Solution. II. A Conception of Osmotic Pressure. Shinkichi Horiba (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 45—57).—A theoretical discussion of the nature and origin of osmotic pressure, in which it is suggested that the contraction of the solvent in solution (see preceding abstract) may be responsible for the effects which are generally attributed to the existence of so-called osmotic pressure. H. M. D.

Rhythmic Diffusion Structures in Gelatin-Salt Jellies. I. W. Moeller (*Kolloid Zeitsch.*, 1917, **20**, 242—250).—In a previous paper (this vol., ii, 132) the author has put forward the view that gelatin jellies contain two substances, one of which, α-gelatin, forms a structural network, the spaces in which are occupied by β-gelatin, which is structureless. It is now suggested that rhythmic changes in the structure of the fibrillar network are responsible for the separation of foreign substances in rhythmically distributed layers. According to this view, the development of the structures known as Liesegang's rings is not dependent on the chemical interaction of substances after diffusion through a jelly medium, and such alternating layers may make their appearance when the substance deposited is that contained in the jelly, and not the product of the reaction of this substance with a second.

Experiments made with gelatin jellies containing sodium chloride show that rhythmic structures are developed when such jellies are brought into contact with solutions of hydrochloric acid. Chemical interaction in the ordinary sense does not take place in this system. It is assumed that the rate of diffusion of the acid is greater in the case of fibrillar systems which are characterised by a radial disposition of the fibril elements than in those systems the structural elements of which are oriented in a direction at right angles to the radial. Forces are thus called into play which indirectly determine a rhythmic alternation in the coagulation of the sodium chloride.

The structures which have been observed under prescribed conditions are illustrated by a series of photographs. H. M. D.

In-, Uni-, and Bi-variant Equilibria. XV. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 999—1006. Compare this vol., ii, 299).—The equilibrium relations in heterogeneous systems are further discussed, and a summary is given of the various possible types of pressure–temperature diagrams. H. M. D.

The Temperature-coefficient of a Heterogeneous Reaction. R. G. VAN NAME (*Amer. J. Sci.*, 1917, [iv], **43**, 449—460).—The influence of temperature on the rate of dissolution of metallic cadmium in an aqueous solution of iodine has been determined by measurements at 0°, 15°, 25°, 35°, 45°, 55°, and 65°. The method used has been described in an earlier paper (A., 1911, ii, 973). The value of the temperature-coefficient for 10° rise in temperature varies from 1·35 for the lowest to 1·19 for the highest temperature interval, and is consequently of the same order of magnitude as the temperature-coefficient for the diffusion of a binary electrolyte. In agreement with this it is found that the curves obtained by plotting the rate of dissolution and the fluidity of the solution against the temperature are of the same type. The rate of increase of the fluidity with temperature is, however, somewhat smaller.

Over the temperature range examined, the velocity of dissolution of the metal is proportional to the product of the fluidity of the solution and the absolute temperature. This relationship is in accord with Einstein's diffusion formula, and the facts generally are regarded as affording evidence in support of the diffusion theory of heterogeneous reaction. H. M. D.

A Contribution to the Energy Theory of Matter. H. STANLEY REDGROVE (*Chem. News*, 1917, **116**, 37—40).—Evidence is put forward in support of the view that additive properties of substances may be evaluated in terms of the number and type of the valency bonds. The substances dealt with by the author are all organic compounds, and for these it is shown that the molecular weight, the molecular heat of combustion, the molecular refractivity, and the molecular volume can be regarded as functions of the number and type of the valency bonds in the molecules.

By a mathematical argument, it is further shown that any property which can be attributed to, or treated as a function of, the number and nature of the constituent atoms can *ipso facto* be attributed to, or treated as a function of, the number and type of the valency bonds. H. M. D.

Inorganic Chemistry.

Volumetric Relationship of the Combination of Hydrogen and Oxygen, $2H_2:O_2$, and the Atomic Weight of Hydrogen. PH. A. GUYE (*J. Chim. Phys.*, 1917, **15**, 208—214).—A theoretical paper in which the volume ratio of the combination of hydrogen and oxygen as found by different methods is critically discussed. On the one hand, the ratios of Scott (A., 1893, ii, 515), 2·00285, and of Burt and Edgar (A., 1916, ii, 427), 2·00288, are compared with the physico-chemically calculated values of Rayleigh, 2·00304, of Jaquerod and Scheuer, 2·00298, of Chappius and of Gray and Burt, 2·00308. The effect of these two sets of values on the atomic weight of hydrogen is considered, and it is concluded that for this value the rounded figure 1·0077 should be adopted. J. F. S.

Preparation of Alkali Percarbonates. ROESSLER AND HASSLACHER CHEMICAL CO. (U.S. Pat., 1225832; from *J. Soc. Chem. Ind.*, 1917, **36**, 712).—Hydrogen peroxide and an alkali carbonate are allowed to react in the presence of a restricted quantity of water, common salt being added to aid the separation of the percarbonate. A silicate of magnesium is employed as a stabilising agent. D. F. T.

Double Salt Formation between Nitrates and Sulphates in Aqueous Solution. A. MASSINK (*Zeitsch. physikal. Chem.*, 1917, **92**, 351—380).—The author has investigated the following systems at the temperatures indicated: (1) $(NH_4)_2SO_4$–NH_4NO_3–H_2O (0°, 30, 70°); (2) K_2SO_4–KNO_3–H_2O (35°); (3) Li_2SO_4–$LiNO_3$–H_2O (25°, 35°); (4) $CuSO_4$–Na_2SO_4–H_2O (20°, 35°); (5) $CuSO_4$–$Cu(NO_3)_2$–H_2O (20°); (6) $Cu(NO_3)_2$–$NaNO_3$–H_2O (20°); (7) Na_2SO_4–$NaNO_3$–H_2O (10°, 20°, 25°, 30°, 34°, 35°); and (8) $CuSO_4$–$Cu(NO_3)_2$–$NaNO_3$–Na_2SO_4–H_2O (20°). The isotherms for long series of mixtures in each case were determined, both solid and liquid phases being analysed in each case. It is shown that the double salts $9Li_2SO_4,LiNO_3,27H_2O$ and $11Li_2SO_4,LiNO_3,17H_2O$ exist at 35°, but not at 25°. The saturation curve of Li_2SO_4,H_2O is composed of two distinct branches. The compound

$$NaNO_3,Na_2SO_4,H_2O$$

exists at a minimum temperature 12·8° where it occurs as the stable solid phase; at 32° it disappears as stable solid phase, although at 35° it still appears as metastable solid phase. The compound $3NaNO_3,4Na_2SO_4$ is stable between 20° and 35°. The compound $3NaNO_3,2Na_2SO_4$ is stable between 30° and 35°. The lowest temperature at which anhydrous sodium sulphate is stable in the system $NaNO_3$–Na_2SO_4–H_2O is found to be 24·2°. In the quaternary system $NaNO_3$–Na_2SO_4–$CuSO_4$–$Cu(NO_3)_2$–H_2O no new double salts were found at 20°, the only compound appearing as solid phase at this temperature being $NaNO_3,Na_2SO_4,H_2O$.

J. F. S.

The Phosphates of Calcium. IV. The Basic Phosphates. Henry Bassett, jun. (T., 1917, **111**, 620—642. Compare A., 1908, ii, 675).—The conditions of equilibrium in the system $CaO-P_2O_5-H_2O$ have been further investigated by experiments covering the region lying between those which are characterised by the existence of dicalcium hydrogen phosphate and calcium hydroxide as stable solid phases. Observations were made at 25°, 100°, and 170—200°. At the lowest temperature, the equilibrium condition is attained only after very long intervals of time.

It is shown that tricalcium phosphate and hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$, are the only two phosphates which can exist in stable equilibrium with an aqueous solution at 25°. This is probably the case at all temperatures.

The ratio of $CaO:P_2O_5$ in the solutions with which hydroxyapatite can exist in stable equilibrium extends over a considerable range, from solutions, on the one hand, which are faintly acid to a point which is quite close to that corresponding with a solution of pure calcium hydroxide. There is no evidence of the existence of phosphates between dicalcium hydrogen and tricalcium phosphate, nor of the formation of solid solutions as stated by Cameron, Seidell, and Bell (A., 1906, ii, 163, 164). It is considered probable that hydroxyapatite is the only calcium phosphate which can exist in stable form under normal soil conditions.

The nature of bone phosphate is discussed, and it is suggested that this represents a mixture of hydroxyapatite and calcium carbonate with small quantities of adsorbed hydrogen carbonates of sodium, potassium, and magnesium. H. M. D.

The Solubility of Calcium Phosphates in Citric Acid. A. A. Ramsay (*J. Agric. Sci.*, 1917, **8**, 277—298).—The author finds that the substances commonly sold as "phosphate of lime" and "Calcii Phosphas B.P." are mixtures of di- and tri-calcium phosphates. The methods generally used for the preparation of calcium phosphate yield a mixture of di- and tri-calcium phosphates and calcium hydroxide. Pure tricalcium phosphate is obtained by acting on calcium oxide with phosphoric acid in the proportion of $3CaO:1P_2O_5$, and separating the precipitate within an hour. So prepared, about 91% of the total phosphoric acid is soluble in 2% citric acid, using the standard method for this determination. This solubility is reduced to 84·5% if 25% of calcium carbonate is first added to the calcium phosphate. Further addition of another 25% of calcium carbonate only reduces the solubility of the phosphoric acid to 84·3%. In this determination, the whole of the excess of calcium is dissolved during the thirty minutes' extraction with the 2% citric acid. Since both tricalcium and dicalcium phosphates are soluble in the 2% citric acid solution, the method of differentiating between these two forms of phosphate by the selective action of this solvent is unsatisfactory (compare preceding abstract). W. G.

An Apparatus for the Purification of Mercury. Harrison E. Patten and Gerald H. Mains (*J. Ind. Eng. Chem.*, 1917, **9**, 600—603).—A detailed description of an apparatus embodying

various suggested processes for the purification of mercury. The metal is broken into fine threads by passage through bolting silk, the threads during their subsequent fall through dilute nitric acid being made the anode of an electrolytic process. The mercury is automatically returned to the top, being raised by a current of air working on the injector principle; during this return journey, some oxidation of impurities occurs, and this effect is increased by having the return tube surrounded with a heating coil. After circulating 300 times, the purified mercury is twice distilled, first in a current of air and then in a vacuum. Most of the mercury lost by dissolving into the acid can be recovered by precipitation as calomel. D. F. T.

A Simple Method for the Purification of Mercury. HORACE BARRATT DUNNICLIFFE (*Chem. News*, 1917, **116**, 41—42).—The apparatus consists of a retort supported in such a manner that the neck is vertical, with the open end protruding into a covered beaker in which the purified mercury is collected. Through the tubulure of the retort passes the stem of a dropping funnel and also a piece of narrow glass tubing.

The mercury to be purified is subjected to a preliminary purification by the usual methods, and is then subjected to distillation in the apparatus. The tap of the dropping funnel is adjusted so that mercury drips into the retort at about the same rate as it is removed by distillation. This occurs at the rate of 400—500 grams per hour. All parts of the apparatus are cleaned by treatment with sodium hydroxide, acids, and dichromate mixture, and then washed with distilled water and dried by a current of dust-free hot air. H. M. D.

Aluminium Production by Electrolysis. The Mechanism of the Reaction. RICHARD SELIGMAN (*J. Inst. Metals*, 1917, **17**, 141—144).—It has generally been assumed that aluminium is formed by the reaction $Al_2O_3 + 3C = 3CO + 2Al$ when a carbon anode is used. Actually the consumption of carbon may be much lower, and analyses of the anode gases, collected by enclosing one of the anodes in a sheet metal bell, show as much as 45·6% of carbon dioxide when the temperature is 945°, the proportion diminishing with rise of temperature. In laboratory experiments, heating externally to avoid excessively high current densities, gases containing more than three volumes of carbon dioxide to one of monoxide have been obtained. It is uncertain whether the reaction should be represented by $2Al_2O_3 + 3C = 4Al + 3CO_2$, or whether the primary anodic product is oxygen, which reacts with the carbon anode in a manner dependent on temperature, current density, rate of removal of gas, and other factors. C. H. D.

Mechanism of the Tempering of Carbon Steels. P. CHEVENARD (*Compt. rend.*, 1917, **165**, 59—62. Compare this vol., ii, 372).—A study of the cooling of carbon steels in hydrogen, nitrogen, or mixtures of these two gases, the velocities of cooling being

varied. The results obtained confirm the conclusions of Portevin and Garvin (compare this vol., ii, 372). Tempering results from a displaced transformation at low temperatures. This transformation is incomplete, and the martensite encloses a certain proportion of the metal in a state stable at higher temperatures. For a given method of cooling, the maximum temperature of annealing, θ_0, and the minimum temperature of tempering, θ_1, are higher and more widely separated the slower is the velocity of cooling. W. G.

Manganese Steels. A. PORTEVIN (*Compt. rend.*, 1917, **165**, 62—65).—By annealing, followed by very slow cooling of steels containing 7% manganese and 0·5—1·0% carbon, it is possible to obtain lamellar perlite with martensite. With a steel containing 12% manganese and 1% carbon, by very slow cooling the co-existence of lamellar perlite and austenite separated by a thin border of troostite can be obtained. By ordinary annealing the whole becomes austenitic. Using a steel containing 9·8% manganese and 0·66% carbon, by slow cooling it was possible to find the complexes troostite–perlite–martensite–austenite, the martensite arising from a polymorphic transformation of the austenite. W. G.

Monoclinic Double Selenates of the Nickel Group. A. E. H. TUTTON (*Phil. Trans.*, 1917, *A*, **217**, 199—235).—This communication deals with the morphology and optical properties of crystals of the four double selenates of the series

$$R_2M(SeO_4)_2,6H_2O,$$

in which M is nickel and R is potassium, rubidium, cæsium, or ammonium. They belong to the large monoclinic isomorphous series of double sulphates and selenates, of which ferrous ammonium sulphate is the most familiar example. Great care has been taken in every case to obtain the most perfect crystals for examination, and their morphological and optical properties have been fully investigated. They belong to the holohedral prismatic class of the monoclinic system, the symmetry plane is the optic axial plane, and, except in the case of the cæsium salt, the double refraction is positive. The dimensions of the optical ellipsoid have been determined in each case.

Potassium nickel selenate: $a:b:c=0·7467:1:0·5059$; $\beta=104°27'$; D_4^{20} 2·559; M.V.=206·14.

Rubidium nickel selenate: $a:b:c=0·7395:1:0·5031$; $\beta=105°20'$; D_4^{20} 2·856; M.V.=216·96.

Caesium nickel selenate: $a:b:c=0·7288:1:0·4993$; $\beta=106°11'$; D_4^{20} 3·114; M.V.=229·17.

Ammonium nickel selenate: $a:b:c=0·7395:1:0·5048$; $\beta=106°17'$; D_4^{20} 2·243; M.V.=216·53.

A careful comparison of the four salts with respect to all the properties subjected to accurate measurement has been made, with the result that the author's previous conclusions regarding the morphotropic relationship between ammonium and the alkali metals is fully confirmed. The axial ratios and molecular volumes of the rubidium and ammonium salts are almost identical; hence

their structural units, the dimensions of which are given by the topic axial ratios, are congruent. For the bearing of these results on the law of valency volumes, see this vol., ii, 244. E. H. R.

Recovery of Molybdenum Residues. VICTOR LENHER and M. P. SCHULTZ (*J. Ind. Eng. Chem.*, 1917, **9**, 684—685).—A description of a method based on the separation of the molybdenum as sulphide.

Waste molybdate liquors are diluted or treated with alkali so that the amount of free nitric acid is reduced to 0·1—0·4%. Hydrogen sulphide is then passed into the solution, preferably warm, and the precipitated molybdenum sulphide is washed and dried, after which it may be converted into the trioxide by roasting.

Ammonium phosphomolybdate is dissolved in sufficient aqueous sodium hydroxide to give a solution just alkaline to phenolphthalein; the liquid, after filtration if necessary, is treated with hydrogen sulphide, and the molybdenum sulphide precipitated by acidifying with dilute hydrochloric acid. D. F. T.

Zirconyl Acid Sulphate. ED. CHAUVENET (*Compt. rend.*, 1917, **165**, 25—28).—A study of the neutralisation of the acid sulphate, $SO_4{:}ZrO,SO_3$, in $N/1000$-solution with $N/1000$-sodium hydroxide gives two sharp changes, the first corresponding with the formation of the normal sulphate and the second with the formation of a basic sulphate, $SO_4{:}ZrO,ZrO_2$. Thus the most stable state of the system ZrO_2 and SO_3 is the latter form. The compounds of the zirconyl radicle have a great tendency to yield compounds of the type $A{:}ZrO,ZrO_2$. W. G.

The Occurrence of Germanium in Missouri and Wisconsin Blendes. G. H. BUCHANAN (*J. Ind. Eng. Chem.*, 1917, **9**, 661—663. Compare A., 1916, ii, 486).—Small quantities of germanium are present both in Wisconsin and Missouri zinc ores and tend to become concentrated in the residues remaining in the retorts, so that oxide of zinc prepared from spelter residues may contain a considerable proportion of germanium.

The method adopted for testing zinc oxide for traces of germanium consisted of mixing 100 grams with 200 c.c. of concentrated hydrochloric acid and distilling to about one-half the volume in a current of chlorine, collecting the distillate by means of a water-cooled condenser. The distillate was diluted with an equal bulk of water and treated with hydrogen sulphide for half an hour; if no other precipitate than sulphur is obtained, germanium is absent. The nature of the precipitate was confirmed by dissolving in boiling water, re-precipitating with hydrogen sulphide in the presence of hydrochloric acid, dissolving the new precipitate in aqueous ammonia, evaporating to dryness, and igniting the residue; the solution of the residue in a little water, on addition of hydrofluoric acid and saturation with potassium chloride, should, if germanium is present, give a bulky, grey precipitate, soluble on heating or on the addition of water. D. F. T.

Mineralogical Chemistry.

Eakleite, a New Mineral from California. ESPER S. LARSEN (*Amer. J. Sci.*, 1917, [iv], **43**, 464—465).—A small specimen labelled "Wollastonite, St. Inez, Calif." in the museum of the University of California was found on optical examination to represent a new species, for which the name *eakleite* is proposed. It is pale pink with a fibrous structure, and resembles pectolite in appearance. D 2·685—2·705; H $6\frac{1}{2}$; fusibility, $2\frac{1}{2}$; readily decomposed by acids with separation of flaky silica. It is optically positive, with a very small axial angle; the direction of extinction (γ) is parallel to the fibres; refractive indices (Na) $\alpha=\beta=1·583$, $\gamma=1·593$. The following mean of two analyses by A. S. EAKLE corresponds with the formula $5CaO,5SiO_2,H_2O$, representing perhaps a calcium pectolite:

SiO_2.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
50·17	1·04	45·45	trace	nil	nil	3·18	98·84

L. J. S.

The Constitution of Melilite and Gehlenite. FRANK WIGGLESWORTH CLARKE (*Amer. J. Sci.*, 1917, [iv], **43**, 476—484).—The recent paper by Schaller on these minerals (A., 1916, ii, 632) is discussed, and the analyses recalculated as mixtures of the following molecules: $Al_4(SiO_4)_6Ca_4Na_4$ (soda-lime-sarcolite), $Al_4(SiO_4)_6Ca_6$ (sarcolite), $Al_2(SiO_4)_6Ca_9$ ('normal melilite'), $Al_4(Si_3O_8)_6Ca_4Na_4$, and $Al_2(SiO_4)_6Ca_6(AlO_2Ca)_6$. The last two of these are hypothetical, the former, a trisilicate, to express the excess of silica over the orthosilicate ratio met with in melilite, and the latter, with the basic univalent group, AlO_2Ca, to explain the deficiency of silica in gehlenite.

These molecules are represented graphically in accordance with the author's theory of the silicates (A., 1897, ii, 50), and the genetic and paragenetic relations of these and other allied minerals (anorthite, garnet, epidote, idocrase, scapolite) are discussed. As substitution derivatives of the normal aluminium orthosilicate, $Al_4(SiO_4)_3$, the following alumosilicic acids are now postulated: $Al_3(SiO_4)_3H_3$ ('trialic' acid, for example, anorthite is calcium 'trialate'); $Al_2(SiO_4)_3H_6$ ('dialic' acid, for example, garnet and sarcolite are calcium 'dialates'); and $Al(SiO_4)_3H_9$ ('unalic' acid, for example, the melilite silicate is calcium 'unalate'). L. J. S.

Analytical Chemistry.

An Automatic Suction Attachment for an Ordinary Pipette. J. P. SCHROEDER (*J. Ind. Eng. Chem.*, 1917, **9**, 687—688).—To the ordinary mouthpiece of the pipette is attached by means of rubber tubing a three-way tap, one of the remaining tubes of which is open to the atmosphere, whilst the other serves for the application of the necessary suction by means of a pump. In order to facilitate the exact filling of the pipette, a groove is filed on the surface of the barrel of the tap across the edges of the bored hole so that the suction may be cut off gradually.

If the pipette is cut short at its graduation mark, the shortened stem being passed through a bung and fitted by this into a wider glass tube, which is then attached to the three-way tap, the pipette cannot be filled beyond the mark, and the necessity for the careful regulation of the suction is reduced. D. F. T.

A Modified Soxhlet Extractor. D. F. TWISS and W. MCCOWAN (*J. Soc. Chem. Ind.*, 1917, **36**, 692).—A description of a glass continuous extraction apparatus, somewhat resembling that of Blount (*Analyst*, 1888, **13**, 127), but with the outer jacket reaching only to a level just above the aperture by which the vapour of the solvent passes into the extraction cup. The apparatus is thereby rendered stronger and the condensation of vapour in the outer jacket is decreased. By restricting the size of the aperture by which the vapour passes from the outer jacket into the inner cup, an excess of temperature in the outer jacket can be maintained sufficient to keep the liquid in the inner cup in steady, quiet ebullition. D. F. T.

A New, Practical Colorimeter. E. MOREAU (*Ann. Falsif.*, 1917, **10**, 235—237).—The apparatus consists of a flat-bottomed, graduated tube of the same internal diameter as the ordinary comparison tubes, which has sealed in near the lower end a lateral tube connected by rubber tubing to a reservoir, containing the standard comparison solution. A known volume of the solution under examination is placed in the comparison tube together with the necessary reagent, and the tube is placed alongside the graduated tube, into which is then allowed to flow the standard solution and reagent, until the depth of colour in the two tubes viewed vertically is identical. The amounts of the constituent to be determined present in the two tubes are inversely proportional to the volumes of liquid used. W. G.

Method of Rendering More Sensitive Colorimetric Analyses. GEORGES LE ROY (*Ann. Falsif.*, 1917, **10**, 208—210).—In the colorimetric analysis of water, for the purposes of estimating the amount of an unstable constituent, such as free chlorine, present in quantity so small as not to be detected by the ordinary

methods, a known, sufficient amount of chlorine is added to the water to bring it within the limits of detection, and then the ordinary colorimetric estimation is performed. W. G.

Potassium Hydrogen Carbonate as an Analytical Standard. G. Bruhns (*Chem. Zeit.*, 1917, **41**, 386—388).—The author confirms the conclusion previously arrived at by Winkler (A., 1915, ii, 647) and Incze (A., 1916, ii, 146) that potassium hydrogen carbonate is a trustworthy analytical standard for all but extremely accurate work. It may be prepared even more simply than these authors suggest by allowing the ordinary "pure" salt in fine powder to remain exposed for several hours in a dry room. Standardised against fused sodium chloride, a sample prepared in this way was found to be correct to 0·02%. Solutions stronger than $N/10$ should not be employed, owing to the tendency to evolve carbon dioxide, which is exhibited by concentrated solutions.

G. F. M.

Theory of the Electrolytic Estimation of the Halogens as Silver Haloids. A. H. W. Aten (*Zeitsch. physikal. Chem.*, 1917, **92**, 320—344).—A theoretical paper in which the theory of the electrolytic estimation of halogens as silver haloids is developed on the basis of the Nernst diffusion theory. The course of the diffusion curves of silver ions and halogen ions is calculated, as well as the quantity of silver haloid which is deposited in the solution and its distribution over the diffusion layer. The form of the theoretical current potential curve for a silver anode in a solution of a haloid is determined, and the fractions of the current which are used in the formation of the silver haloid on the anode and in the solution are evaluated. From the ratio of these two fractions the smallest possible error of the analysis is calculated. It is thus shown that under suitable conditions the estimation of chloride is very accurate, and that of the other haloids much more so. The current potential curves for chlorides, bromides, and iodides with a silver anode have been experimentally determined and compared with the theoretically developed curves. A sufficient agreement between the two sets of curves is demonstrated. J. F. S.

Estimation of Free Chlorine in Hypochlorite Solutions. F. Dienert and F. Wandenbulke (*Compt. rend.*, 1917, **165**, 28—29).—Working with dilute solutions containing not more than 0·5 gram of free chlorine per litre, the following method gives a ready means of estimating the free chlorine. Five c.c. of the hypochlorite solution are diluted to the above degree with water, and ammonium sulphate to the extent of at least 150 parts for every part of free chlorine is added and a few crystals of potassium iodide. The iodine set free is then titrated with standard arsenious acid solution. W. G.

Microreactions of the Perchloric Ion. G. Denigès (*Ann. Chim. anal.*, 1917, **22**, 127—128).—Use is made of the characteristic properties of the perchlorates of certain alkaloids (compare

this vol., ii, 345) for the detection of the perchloric ion. Either a 1% solution of strychnine sulphate in water or a 2% solution of brucine in dilute acetic acid, or a 2% solution of morphine hydrochloride is used, one drop being added to a drop of the solution under examination on a microscope slide. The resulting crystals are examined under the microscope. With strychnine, 1 part of perchloric ion in 1000; with brucine, 2—3 parts in 1000, and with morphine, 5 parts in 1000 can be detected. W. G.

Argentometric Estimation of Bromides and Iodides. I. M. Kolthoff (*Pharm. Weekblad*, 1917, **54**, 761—766).—Iodides can be estimated in the presence of 20% of chlorides and 2% of bromides by silver nitrate in sulphuric acid solution, with starch iodide as indicator. A. J. W.

Volumetric Estimation of Sulphur in Pyrites. T. J. I. Craig (*Chem. News*, 1917, **115**, 253—255, 265—268).—A method is described for the volumetric estimation of sulphur in pyrites based on its oxidation to sulphuric acid by means of aqua regia, or preferably nitric acid and bromine, and titration with standard alkali hydroxide after the removal of all the other acid ions from the solution. It is shown that nitric acid is completely eliminated from the aqua regia solution of pyrites by evaporating to dryness twice with hydrochloric acid, and finally drying for an hour at 110°, whilst from the nitric acid–bromine solution two evaporations to dryness, followed by an hour's heating at 110°, is sufficient to remove both nitric acid and bromine. Where hydrochloric acid is present, it can only be completely eliminated by treating the solution with silver oxide, the alternative being to estimate it with standard silver nitrate and make the requisite allowance in the subsequent titration of the sulphuric acid. When arsenic acid is present it is shown to be practically all eliminated by the precipitated ferric hydroxide, and hence does not interfere with the titration. The procedure recommended is briefly as follows: 10 grams of pyrites are treated with 30% nitric acid, the reaction mixture cooled to 50°, treated with 5 c.c. of bromine, and boiled until no more brown fumes are liberated. Nitric acid is eliminated as above described, and the residue dissolved in water and made up to 250 c.c. Of this solution 25 c.c. are boiled with a known excess of *N*-sodium hydroxide and the solution made up to 200·25 c.c. (0·25 c.c. to allow for the volume occupied by the ferric hydroxide). After filtration, an aliquot portion is titrated to neutrality with phenolphthalein as indicator. The results obtained are claimed to be closely in accord with those obtained by the more elaborate gravimetric method. The paper includes a short historical summary of the various methods suggested for the estimation of sulphur in pyrites. G. F. M.

The Estimation of Free Sulphur Trioxide in Fuming Sulphuric Acid by Titration with Water. R. G. Parker (*J. Soc. Chem. Ind.*, 1917, **36**, 692—694).—The author finds that

the amount of sulphur trioxide in fuming sulphuric acid can be accurately estimated by titrating a weighed quantity of the acid in a stoppered cylinder with water until no further fuming occurs when air is blown through a glass tube on to the surface of the liquid. D. F. T.

Sulphuric Acid for [Use in] the Nitrate Test. H. D. STEENBERGEN (*Chem. Weekblad*, 1917, **14**, 647—648).—Sulphuric acid for testing for nitrates in milk can be freed from nitric acid by agitation with mercury in a Lunge nitrometer. A. J. W.

Estimation of Nitrate in the Presence of Chlorides. W. F. GERICKE (*J. Ind. Eng. Chem.*, 1917, **9**, 585—586).—In order to avoid the undesirable rise in temperature on the addition of sulphuric acid to the dry mixture of nitrates and chlorides in the colorimetric estimation of nitrates, the author recommends the addition of sulphuric acid and the phenoldisulphonic acid reagent before the evaporation of the solution, the mixture being evaporated subsequently, the temperature of the final stages of the evaporation being preferably below 70°. When the solution has attained the correct concentration as judged by the colour, it is diluted, cautiously neutralised, and compared in the colorimeter with a standard in the usual manner. D. F. T.

The Phenolsulphonic Acid Method for Nitrates in Waters High in Magnesium Salts. M. STARR NICHOLS (*J. Ind. Eng. Chem.*, 1917, **9**, 586—587).—In the estimation of nitrates by the above process the presence of iron and magnesium salts may cause complications by the formation of a precipitate on the addition of the alkali hydroxide. The author therefore advises the filtration of the solution before the colour comparison if iron is present, but in the absence of iron salts it is sufficient after the neutralisation to add the requisite quantity of ammonium chloride to maintain the magnesium hydroxide in solution, the dilution being effected subsequently. D. F. T.

A New Method for the Destruction of Tissues for the Detection of Arsenic and the Examination of their Ashes. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1917, **165**, 11—16).—The tissues or organs are heated in an oven at 300° until they become friable, when they are ground up and mixed with 2—3% of their weight of calcium oxide, which is then slaked with a little water. The mixture is heated in a flat porcelain dish in a furnace at a temperature such that the base of the muffle shows a dull red. At the end of two hours the white, porous ashes are powdered, extracted with water, and acidified with a few drops of sulphuric acid. The mixture is boiled and filtered, the filtrate being evaporated until white fumes appear. The residue is taken up with water and transferred to a Marsh's apparatus, in which the usual estimation of arsenic is made. The results obtained are accurate to 0·001 mg. of arsenic in 100 grams of tissue. The ash

could also be used for the detection of borates, silicates, phosphates, fluorine, nickel, silver, or copper. W. G.

A Rapid Method for the Estimation of Water-soluble Arsenic in Lead Arsenate. H. A. SCHOLZ and P. J. WALDSTEIN (*J. Ind. Eng. Chem.*, 1917, **9**, 682—683).—A description of a method closely similar to that of Gray and Christie (this vol., ii, 102), which the authors have used satisfactorily for three years.

D. F. T.

The Influence of Calcite Inclusions on the Estimation of Organic Carbon in Soils. EDMUND C. SHOREY and WM. H. FRY (*J. Ind. Eng. Chem.*, 1917, **9**, 588—589).—Attention is directed to the fact that with soils containing calcite included in quartz grains the copper oxide combustion method for the estimation of organic carbon will give values higher than those obtained by the wet combustion method with sulphuric acid and potassium dichromate because the former will cause the liberation of carbon dioxide from the included calcite by disruption of the grains. The lower values for organic carbon frequently obtained by the wet process may therefore not always be due to the greater accuracy of the copper oxide method of combustion. D. F. T.

Acidosis. II. Estimation of Carbon Dioxide and Carbonates in Solution. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **30**, 347—368).—The method is based on that of Swanson and Hulett (A., 1916, ii, 48), in which, however, after shaking the solution of carbon dioxide in a vacuum, the water, instead of the gas, is removed from the chamber and the volume of liberated carbon dioxide then measured over mercury in a calibrated tube at the top of the same chamber. The apparatus consists essentially of a 50 c.c. pipette with three-way cocks at the top and bottom, and a 1 c.c. scale on the upper stem divided into 0·02 c.c. divisions. The pipette is connected at the bottom with (i) a chamber into which the solution is drawn off after the carbon dioxide has been extracted from it, and (ii) a tube to permit the entrance of mercury and subsequent release of the vacuum and measurement of the extracted carbon dioxide. Corrections for the volume of air dissolved in the solution which enters the apparatus and for that fraction of the total carbon dioxide which remains unextracted because of its solubility in water are calculated, and can be applied by a single factor, which can be read off at once from a table included in the text.

The apparatus is designed especially for the analysis of 1 c.c. samples of blood plasma, but is applicable to aqueous solutions in general, as well as for the estimation of dissolved gases other than carbon dioxide. The entire analysis is performed at the ordinary temperature, requires about three minutes, and without special precautions is capable of accuracy to within 1% of the amount estimated.

A micro-apparatus designed on a similar principle is also

described. With it the carbon dioxide content of 0·2 c.c. of blood plasma can be estimated with an accuracy of 1 volume per cent.
H. W. B.

Use of the van Slyke Carbon Dioxide Apparatus for the Estimation of Total Carbon Dioxide in Sea-water. J. F. McCLENDON (*J. Biol. Chem.*, 1917, **30**, 259—263).—The author describes the adaptation of the van Slyke apparatus (see preceding abstract) for the estimation of carbon dioxide in sea-water, together with the method for applying the numerous necessary corrections to the results. H. W. B.

Standardisation of a New Colorimetric Method for the Estimation of the Hydrogen-ion Concentration, Carbon Dioxide Tension, and Carbon Dioxide and Oxygen Content of Sea-water, of Animal Heat, and of Carbon Dioxide of the Air, with a Summary of Similar Data on Hydrogen Carbonate Solutions in General. J. F. McCLENDON (*J. Biol. Chem.*, 1917, **30**, 265—288. Compare this vol., i, 105, and preceding abstract; McClendon and Magoon, A., 1916, ii, 513).—The author gives a detailed account of the methods for estimating carbon dioxide and hydrogen-ion concentration in various fluids by means of slight modifications of apparatus previously described (*loc. cit.*). H. W. B.

The Correction Values in the Estimation of Free Carbon Dioxide in Water. L. W. WINKLER (*Zeitsch. nahr. Genussm.*, 1917, **33**, 443—446. Compare A., 1915, ii, 795).—As a result of the indication by Tillmans and Heublein (this vol., ii, 332) of certain errors in the author's earlier paper (*loc. cit.*) describing his modification of Trillich's method for the estimation of dissolved carbon dioxide by titrating with sodium carbonate solution, the author has re-determined the values of the correction necessary for the adjustment of the titration result. D. F. T.

The Chemical Examination of Natural Brines. O. R. SWEENEY and JAMES R. WITHROW (*J. Ind. Eng. Chem.*, 1917, **9**, 671—675).—A tentative suggestion as to a standard method of procedure for the chemical examination of natural brines. Conditions are suggested for the collecting of the sample, the determination of the amount of deposit formed on æration, the determination of specific gravity, and the estimation of total solids, silica, iron and aluminium, calcium, magnesium, barium and strontium, ammonia, sulphuric acid, sodium and potassium, chlorine and bromine. For bromine a colorimetric method is recommended, based on the liberation of bromine by chlorine and comparison of the carbon tetrachloride extract with a similar extract obtained from a solution of known bromine content. D. F. T.

The Estimation of Strontium and Lithium in Water. S. D. AVERITT (*J. Ind. Eng. Chem.*, 1917, **9**, 584—585).—For the

estimation of strontium the author recommends the separation of calcium and strontium together as oxalates, with subsequent weighing as oxides; the mixture is then dissolved in hydrochloric acid, reprecipitated as oxalates, and the proportion of strontium deduced by calculation from the quantity of standard potassium permanganate solution required for oxidation of the oxalic acid in combination with the metals.

For the estimation of lithium also, an indirect method is suggested. The weighed mixture of chlorides of lithium, sodium, and potassium is dissolved in water and the potassium and chlorine are estimated in aliquot fractions; by calculation it is then possible to arrive at the proportion of lithium in the original mixture.

D. F. T.

A New Method of Separating Zinc from Cadmium and the Iodometric Estimation of the Latter. ERIC JOHN ERICSON (*J. Ind. Eng. Chem.*, 1917, **9**, 671. Compare A., 1913, ii, 624).—In the analysis of spelter it is possible to separate the bulk of the zinc from cadmium by crystallisation as zinc sulphate. The filtrate after the removal of the lead from 19·2 grams of spelter (*loc. cit.*) is evaporated until solid commences to separate, then 50 c.c. of dilute sulphuric acid (1 : 3) are added, and the solution is reduced to a volume of 80—100 c.c. by boiling. After keeping overnight the major part of the zinc has crystallised as sulphate; the combined clear solution and washings are diluted, treated with hydrogen sulphide, and the cadmium is then estimated by any suitable method, the addition of excess of $N/10$-iodine and dilute hydrochloric acid, followed by the titration of the remaining iodine with thiosulphate, being quite satisfactory.

The same principle for removing the bulk of the zinc from cadmium can also be applied in the examination of the cadmium content of zinc ores.

D. F. T.

Estimation of Small Amounts of Mercury in Organic Substances. SVEND LOMHOLT and J. A. CHRISTIANSEN (*Biochem. Zeitsch.*, 1917, **81**, 356—379).—Details of the following processes are described. I. Destruction of organic matter. In the case of urine this is carried out by potassium permanganate in the presence of sulphuric acid. In the case of fæces and organs, a preliminary destruction with nitric acid is first carried out. II. Precipitation by hydrogen sulphide. A small amount of copper sulphate is first added to increase the bulk of the precipitate. III. Filtration. A special form of filter-funnel is figured and described. IV. Solution of the sulphide in nitric and hydrochloric acids. V. Electrolysis of the solution of the sulphides in acid. The mercury is deposited on a small gold electrode in an electrolysis apparatus, which is figured and described. VI. The weighing of the mercury. The gold electrode, when only small amounts of mercury are present, is weighed on a Nernst microbalance. To obtain successful results, attention

must be paid to certain details which are described by the authors. S. B. S.

Use of the Platinised Anode of Glass in the Electrolytic Estimation of Manganese. F. A. Gooch and Matsusuke Kobayashi (*Amer. J. Sci.*. 1917, [iv], **44**, 53—56).—Anodes, prepared by painting lead glass tubes with an emulsion of chloroplatinic acid in glycerol and then heating to the softening point of glass, have been used for the electrolytic estimation of manganese in solutions of manganous sulphate. Using a current of about 1·7 amperes and 18·3—10·3 volts with an anode of approximately 25 sq. cm. surface which was rotating 150 times per minute, the whole of the manganese was deposited as dioxide in about two and a-half hours. The manganese dioxide was dissolved in a mixture of sulphuric and sulphurous acids, dried at 450°, and weighed as anhydrous manganous sulphate. The method appears to give very accurate results. Some experiments, made to ascertain the influence of certain reagents on the electrolysis, are also described. Thus, when to an electrolyte containing 0·1 gram of manganese per 100 c.c., 5 c.c. of acetic acid and 0·5 gram of chrome alum are added, the complete deposition of the hydrated dioxide required two and a-half hours. If instead of these substances 5 c.c. of alcohol and 2 grams of ammonium sulphate are used, the electrolysis requires three and a-half hours. J. F. S.

Electrolytic Valuation of Iron Sulphide. Howell Williams (*Chem. News*, 1917, **116**, 13—14).—One gram of the finely divided sample is placed along with 5 grams of pure zinc in a 500 c.c. flask and treated with 100 c.c. of dilute hydrochloric acid (D 1·1). The hydrogen sulphide evolved is led into two Fresenius flasks, each containing 50 c.c. of a solution of cadmium chloride (100 grams per litre). A safety flask containing 25 c.c. of the same solution is attached to the end of the apparatus. When the whole of the hydrogen sulphide has been absorbed, the precipitated cadmium sulphide is collected and washed with warm water. The precipitate is then transferred to a 500 c.c. beaker and dissolved in dilute hydrochloric acid. The cadmium is precipitated by a slight excess of sodium hydroxide and the hydroxide redissolved by the addition of a concentrated solution of potassium cyanide. The solution is now diluted to 120 c.c. and electrolysed by a current of 5 amperes and an *E.M.F.* of 5·5 volts, a rotating cathode being employed. The electrolysis is generally complete in ninety minutes. The results obtained are slightly low, approximating in carefully conducted test experiments to about 0·5% below the theoretical value. J. F. S.

Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys. I. W. R. Schoeller and A. R. Powell (*Analyst*, 1917, **42**, 189—199. Compare A., 1916, ii, 346).—Nickel and

cobalt are practically quantitatively precipitated as hexamminenickelous iodide, $[Ni(NH_3)_6]I_2$, and hexamminecobaltous iodide, $[Co(NH_3)_6]I_2$, respectively, by an excess of potassium iodide sufficient to give a 4% solution of the precipitant, and in presence of ammonia (D 0·880) in sufficient quantity to form at least two-thirds of the total bulk of the solution. Owing to the slight solubility, very small quantities fail to precipitate within 10—15 mins., but although the reagent is not suitable for estimating traces of nickel and cobalt, results of considerable accuracy, checked against electrolytic and other estimations, were obtained by the application of the method to the assay of ores and alloys. The behaviour of other metals towards potassium iodide and ammonia was studied in numerous cases. Iron and other tervalent metals in presence of excess of tartaric acid are not precipitated, but bivalent iron gives a white precipitate of hexammine ferrous iodide. Manganese and copper are either completely or partly precipitated, but may be easily removed from the precipitate subsequently, the copper as cuprous iodide when the precipitate is treated with hydrochloric acid, and the manganese by reprecipitation of the nickel and cobalt with hydrogen sulphide in presence of acetic acid. It was found advisable to remove alkaline earth metals by preliminary treatment with sulphuric acid. The same applies to lead, but since lead iodide is soluble in ammoniacal tartrate solution, this step is not absolutely necessary. Magnesium and arsenic are without influence on the assay unless present together, when they would interfere owing to precipitation of magnesium ammonium arsenate. Sulphur is oxidised to sulphate and presents no real objection unless a large excess is present, when potassium sulphate might crystallise out from the ammoniacal liquor on addition of the potassium iodide. Excess of hydrochloric acid is to be avoided, as the iodide precipitates are slightly soluble in ammonium chloride.

In carrying out the separation, the precipitates must be washed with a solution containing 800 c.c. of strong ammonia and 40 grams of potassium iodide per litre, as water causes decomposition into basic salts. The washed precipitate is then dissolved in hydrochloric acid with a little sulphurous acid, and after filtration the cobalt is precipitated as cobalt ammonium phosphate and the nickel in the filtrate titrated with cyanide.

Details of the methods adopted with a number of typical alloys and ores, together with the results obtained by various methods, are given in the paper. G. F. M.

[Estimation of Tin in Tin-plate.] I. M. KOLTHOFF and L. B. VAN LOHUIZEN (*Pharm. Weekblad*, 1917, **54**, 718—720).—To estimate tin in scrap tin-plate, a cross-section sample of 50 grams is oxidised by nitric acid to stannic oxide. A portion of the product is reduced to metal in a Rose crucible by hydrogen, the tin dissolved in hydrochloric acid, and estimated by iodine.

A. J. W.

Phosphor-tin and a Volumetric Method for its Analysis. RICHARD EDWIN LEE, W. H. FEGELY, and FRANK H. REICHEL (*J. Ind. Eng. Chem.*, 1917, **9**, 663—668).—A record of the development of a method for the analysis of the alloy phosphor-tin. The procedure adopted is to dissolve the alloy in hydrochloric acid in the first of a series of flasks from which the air has been expelled by a current of coal gas or carbon dioxide. The phosphorus is liberated as phosphine, which is absorbed in the next three flasks by potassium permanganate solution acidified with nitric acid, the phosphoric acid produced being then precipitated as phosphomolybdate; the precipitate is dissolved in aqueous ammonia and the solution titrated with $N/10$-potassium permanganate after reduction by means of a Jones reductor.

The stannous chloride resulting from the action of the hydrochloric acid on the phosphor-tin is estimated by the addition of an excess of ferric chloride followed by titration of the ferrous iron produced with a standard solution of potassium dichromate.

D. F. T.

Estimation of Naphthalene [in Coal Gas] by Picric Acid. KNUBLAUCH (*J. Gasbeleucht.*, 1916, Oct. 14th and 21st; from *J. Soc. Chem. Ind.*, 1917, **36**, 702).—Details are given of a method for estimating naphthalene by passing sufficient of the gas to yield approximately 0·08 gram naphthalene through two wash-bottles containing a 1% solution of picric acid; if the gas contains much ammonia, the picric acid solution for the first wash-bottle is mixed with an equal bulk of sulphuric acid slightly above $N/2$-concentration. The precipitated naphthalene picrate is removed by filtration, washed with a 0·2% solution of picric acid, and finally titrated with $N/10$-alkali and methyl-orange, a correction being made for the picric acid solution absorbed by the filter paper.

D. F. T.

Estimation of Nitrotoluenes. E. KNECHT (*J. Soc. Chem. Ind.*, 1917, **36**, 694).—A reply to Colver and Prideaux (this vol., ii, 340) reasserting that titanous chloride is a convenient reagent for the accurate estimation of aromatic nitro-compounds.

D. F. T.

Estimation of Phenol in Crude Carbolic Acid and Tar Oils. JOHN MORRIS WEISS and C. R. DOWNS (*J. Ind. Eng. Chem.*, 1917, **9**, 569—580).—A detailed description of a method for the accurate estimation of phenol in mixtures with cresols, higher phenols, and neutral oils. In order to obtain satisfactory results, it is necessary that the prescribed directions should be followed closely. The following is a brief summary of the process.

The tar acids are removed from the oil (sufficient to yield approximately 300—350 grams of tar acids) by repeated extraction with 100 c.c. of 20% sodium hydroxide solution, the oil having been previously distilled if dirty. After five extractions with

100 c.c. of benzene, the alkaline solution is rendered slightly acid with sulphuric acid; after settling, the aqueous layer is drawn off and is extracted thrice with 100 c.c. of benzene; phenols are then removed from this by treatment three times with 25 c.c. of 20% sodium hydroxide solution, and, after liberation by the addition of acid, are added to the main bulk of tar acids, the combined weight giving the quantity of wet, crude acids from the tar taken. This yield of acids is then distilled under specified conditions, and fractions are collected up to 190° and between 190° and 202°, the latter fraction being then redistilled and the portion passing over below 197° is added to the distillate obtained up to 190°. This combined distillate is weighed, and further tested as to its solidifying point and specific gravity, the percentage of phenol present being then calculated from a set of curves. In some cases it may be necessary to mix the combined distillate up to 197° with a known proportion of pure phenol before the specific gravity and solidifying point allow definite readings from the curves.

D. F. T.

Direct Polarisation of Sugar Solutions without a Preliminary Treatment with Basic Lead Acetate or the Normal Acetate. H. PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **35**, 138—140).—The juices from the second carbonation, the sulphited juices, and the syrup solutions in the beet-sugar industry are generally but little coloured. These need not be defecated, but can be polarised directly after clarification by simple filtration with or without the use of kieselguhr.

W. G.

Fehling's Solution in the Estimation of Blood-sugar. H. McGUIGAN (*Journ. Lab. Clin. Med.*, 1917, **2**, 514—516; from *Physiol. Abstr.*, 1917, **2**, 248).—The danger of utilising a too strongly alkaline Fehling's solution in the determination of blood-sugar is pointed out. Low results are due to the incomplete precipitation of the copper in such cases. The best results are obtained by making the solutions as follows: (1) 34·65 grams of copper sulphate in 1 litre of distilled water; (2) 173 grams of Rochelle salt and 125 grams of sodium hydroxide, made up to 1 litre.

G. B.

Composition of Menhaden Oil Fatty Acids. E. TWITCHELL (*J. Ind. Eng. Chem.*, 1917, **9**, 581—584).—In order to test the applicability of his m. p. method for the determination of the composition of mixtures of fatty acids (A., 1914, ii, 685), the author has investigated the constituents of menhaden oil. The principle on which the procedure is based is that the m. p. of any pure fatty acid will be lowered by the addition of a mixture of other fatty acids, but that any quantity of the first acid present in the mixture will not contribute to the depression. Using a

mixture of 80 parts of a pure acid with 20 of another or of a mixture of others, the average depression is approximately 4°.

In the present investigation, the amount of this depression was directly determined for myristic acid and arachidic acid, the m. p.'s of which were then examined after the addition of the usual proportion of hydrogenated menhaden oil and of the solid fatty acids separated from menhaden oil. The results show that myristic acid is present both in the hydrogenated and in the original oil, but that arachidic acid, although a constituent of the acid mixture from hydrogenated menhaden oil, is not present in the original oil. Arachidic acid therefore must be formed by the reduction of an unsaturated acid in menhaden oil. As a result of this and the previous investigation (*loc. cit.*), the mixture of fatty acids from menhaden oil includes palmitic acid, 22·7%; myristic acid, 9·2%; stearic acid, 1·8%; unsaturated C_{18} acids, 24·9%; unsaturated C_{20} acids, 22·2%; unsaturated C_{22} acids, 20·2%. D. F. T.

The Estimation of Hydroxy-fatty Acids. F. Hodes (*Chem. Zeit.*, 1917, **41**, 492).—In the analysis of fats and oils, it is customary to extract the fatty acids with ether or light petroleum, but under these conditions hydroxy-acids may remain undissolved. For the purpose of dissolving these, a boiling mixture of equal volumes of chloroform and alcohol (96—100%) is advised instead of the absolute alcohol commonly recommended.

D. F. T.

Citric Acid and Tartaric Acid. T. C. N. Broeksmit (*Pharm. Weekblad*, 1917, **54**, 686—687).—Citric acid and malic acid are oxidised by a solution of potassium permanganate in acetic acid to acetone, which can be identified by the iodoform test. The two acids can be distinguished by the fact that barium citrate can be crystallised.

The acetone reaction is applicable to the detection of citric acid in tartaric acid and in lemonade syrup. The presence of tartaric acid in citric acid and in lemonade syrup can be proved by the formation of potassium hydrogen tartrate. A. J. W.

Quantitative Test for Uric Acid in Urine. A. Angiolani (*Policlinico*, 1917, **24**, 415; from *Physiol. Abstr.*, 1917, **2**, 266).—Two hundred and fifty c.c. of urine are mixed with 10 c.c. of concentrated hydrochloric acid and kept for twenty-four hours. The crystals are filtered off, dissolved in 20 to 25 c.c. of 10% potassium hydroxide, acidified with sulphuric acid, and titrated with permanganate. G. B.

Estimation of Unsaponifiable Matter in Oils, Fats, and Waxes. John M. Wilkie (*Analyst*, 1917, **42**, 200—202).—To obviate certain difficulties in the estimation of unsaponifiable matter

in oils, etc., such as emulsification during the extraction with ether, the following procedure is recommended: 5 grams of the sample are saponified with 12·5 c.c. of $2N$-absolute alcoholic potassium hydroxide, transferred to a separator with 50 c.c. of water so as to give a concentration of about 20% by volume of alcohol, and extracted successively with 40, 30, and 30 c.c. of ether. Separation is rapid, and the united ethereal extracts are run into a separator containing 20 c.c. of water, which without shaking is first run off before washing the ethereal solution by shaking vigorously with 2, 5, and 30 c.c. of water. The washed extract is evaporated and weighed. The unsaponifiable matter in waxes being but sparingly soluble in ether, it is recommended that only 0·5 gram be taken and mixed with 4·5 grams of castor oil. The above operation is carried out on the mixture, using, however, only 40 c.c. of water at 30° to dilute the alcoholic solution and extracting with 50, 40, 40, and 30 c.c. of ether. A correction is then applied for the known unsaponifiable content of the castor oil. G. F. M.

Estimation of Formalin. G. A. STUTTERHEIM (*Pharm. Weekblad.*, 1917, **54**, 716—717).—Formalin can be estimated by determining the refractive index of the solution. The values of this constant for whole number percentages from 1 to 35 at 17—18° are given, the mean increase for each per cent. being 0·00111.

A. J. W.

The Practical Methods for the Detection and Estimation of "Saccharin" in Foodstuffs. A. BONIS (*Ann. Falsif.*, 1917, **10**, 210—218).—A résumé of the literature on the extraction, purification, identification, and estimation of "saccharin." W. G.

Comparative Examination of the Methods Proposed for the Estimation of the Glycyrrhizin in Liquorice Root and in Succus Liquiritiæ. ARMIN LINZ (*Arch. Pharm.*, 1916, **254**, 65—134, 204—224).—All methods recorded from 1800 to about 1880 deal mainly with the isolation of the substance characteristic of liquorice root and Spanish liquorice, and have little or no quantitative value. Subsequently to this date, many investigators, following Rump's lead, proposed different methods for the estimation of glycyrrhizin, the amount of this substance being regarded as a criterion of the quality of a liquorice. It is only within the last ten years that the importance has been emphasised, rightly, of also estimating the amount of sugar, in order that adulteration of a liquorice with sugar may be detected.

Since the amount of glycyrrhizic acid varies between wide limits, not only in different kinds of liquorice, but even in one and the same kind at different times, the author has used always the same liquorice throughout his series of comparative experiments on the trustworthiness of the twenty-seven methods proposed for the estimation of glycyrrhizic acid. In any method, attention must be given to the following points: (1) the influence of the liquid

employed as a solvent of the liquorice; (2) the nature of the acid used as the precipitant; (3) the solubility of glycyrrhizic acid in water and in the precipitant, and the loss caused thereby; and (4) the purity of the glycyrrhizic acid when brought to the stage of weighing. All the methods are criticised from these four points of view, and the author draws the conclusion that no one of them is really trustworthy, mainly on account of the impossibility of isolating the glycyrrhizic acid in a pure state. Details are given of a method proposed by the author, which, although tedious and not strictly trustworthy, is less inaccurate than any other previously brought forward.

A tabulated list of the literature on the subject from 1808 to 1913 is given, together with a classified list of the results obtained by the twenty-eight methods discussed in the paper. C. S.

Exact Estimation of Atropine. H. BAGGESGAARD RASMUSSEN (*Ber. Deut. Pharm. Ges.*, 1917, **27**, 193—201).—The precipitation of the sparingly soluble salt, $4C_{17}H_{23}O_3N,SiO_2,12WO_3,2H_2O,4H_2O$, by the addition of a slight excess of silicotungstic acid to an acid solution of atropine or its isomerides is made the basis of a quantitative estimation. The belladonna, leaves or extract, is treated with ammonia and ether, and the alkaloids in the ethereal extract are transferred to aqueous solution as hydrochlorides, and precipitated by the addition of silicotungstic acid in about 10% excess. After keeping eight hours, the precipitate is collected on a Gooch crucible, washed with 1% hydrochloric acid, ignited, and weighed. The weight of the inorganic residue multiplied by 0·4067 gives the weight of atropine, to which a correction of 0·0054 gram must be added for every 100 c.c. of the solution in which the precipitation took place. Although the weight of the precipitated salt does not bear an absolutely constant ratio to that of the ignited residue, its nitrogen content is found to do so within the limits of experimental error, from which it is concluded that only atropine or its isomerides are precipitated in the silicotungstate and subsequently estimated. G. F. M.

The Estimation of Nicotine in Tobacco Extract. TH. SV. THOMSEN (*Chem. Zeit.*, 1917, **41**, 476).—Evidence is adduced indicating that the method of Kissling is more trustworthy than that of Ulex for the estimation of nicotine in tobacco extract. The two possible errors in the latter method, viz., the loss of nicotine before distillation and the formation of ammonia during distillation, are not necessarily of equal dimensions, and the production of ammonia may be much more than equivalent to the loss of nicotine, so that the titration of the distillate may give rise to high results. D. F. T.

The Estimation and Nature of Urochromogen. MORIZ WEISS (*Biochem. Zeitsch.*, 1917, **81**, 342—355).—Urochromogen can be estimated in urine by two methods. Either the urochrome

can be formed by oxidation by permanganate and the amount thus produced can be estimated colorimetrically, or the amount of $N/100$-permanganate necessary to produce the maximal amount of urochrome can be determined by a method described in detail by the author. Pauly's reaction with diazobenzenesulphonic acid in alkaline solution has been applied by the author with Sobolev to the quantitative estimation of histidine (A., 1914, ii, 155). It is shown, however, that the reaction when given by urine is not due to histidine alone, but chiefly to the proteic acid fraction. Urochromogen also gives the reaction, but experiments are quoted which indicate that it is not to this substance in the urine to which the reaction is mainly due. The view is expressed that urochromogen contains a pyrrole nucleus. S. B. S.

The Detection of Blood in Urine, Fæcal Matters, and Pathological Fluids. THEVENON and ROLLAND (*J. Pharm. Chim.*, 1917, [vii], **16**, 18—19).—To 3—4 c.c. of the urine an equal volume of a 5% alcoholic solution of pyramidone is added and 6—8 drops of dilute acetic acid (1 in 3). The mixture is shaken and 5—6 drops of hydrogen peroxide (12 vols.) are added. According to the amount of blood present, an intense violet or bluish-violet coloration develops more or less rapidly. Fæcal matter is triturated with water and filtered, and the filtrate used for the test. This reagent is just as sensitive as Meyer's reagent. W. G.

Simplified Preparation of the Reagent with Phenolphthalein for the Detection of Blood in Urines. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1917, [vii], **16**, 20).—Meyer's reagent is more simply prepared by using sodium hyposulphite instead of powdered zinc as a reducing agent. Phenolphthalein (2 grams), potassium hydroxide (20 grams), and water (120 c.c.) are warmed together, and to the hot mixture 3 grams of sodium hyposulphite are added. The whole is boiled until the liquid is colourless, when it is allowed to cool, and is then ready for use. W. G.

General and Physical Chemistry.

The Relation between Density and Optical Refraction. V. Rosický (*Zeitsch. Kryst. Min.*, 1914, **54**, 189; from *Rozpravy české Akademie, Prague*, 1911, **20**, No. 5, 8 pp.).—A new method is proposed for inquiring into the relationship between the densities of crystals and their principal refractive indices. The method consists in comparing the values of the expressions F/d, R/d, where F and R are the volumes of the Fresnel ellipsoid and the optical indicatrix respectively, d being the density. It appears that, in isomorphous and symmorphous groups, R/d remains fairly constant, whilst F/d decreases with increasing molecular weight. The morphological difference between anhydrite and the barytes group is accompanied by a corresponding difference in the values of R/d. In the case of polymorphous substances, the values of R/d and F/d for the different modifications are closely related, the value of the latter expression diminishing with increasing density.

E. H. R.

Phenomena Relating to the Spectra of Hydrogen and Helium. T. R. Merton and J. W. Nicholson (*Phil. Trans.*, 1917, *A*, **217** 237—278).—The spectra of hydrogen and helium have been examined with a view to the determination of the relative intensities of the lines under different conditions of excitation.

The method employed is essentially the same as that which has been previously used (compare A., 1916, ii, 461) in the determination of the distribution of intensity in broadened spectral lines, and involves the use of a neutral-tinted glass wedge cemented to a similar wedge of colourless glass so as to form a plane-parallel plate. The spectra are photographed through this plate, which is placed in front of the slit of the spectrograph. The photographs obtained under these conditions consist of lines which are dark along the edge corresponding with the thin end of the neutral-tinted wedge and fade away towards the region which corresponds with the thicker end of the wedge. The lengths of the lines on the plate thus correspond with their intensities, and the measurement of these lengths has been accomplished by preparing positives from the negatives and enlarging these on to bromide paper through a ruled "process" screen. By this means an enlarged negative is obtained, in which the lines are made up of minute dots, and the length of any line can be determined by the position of the last visible dot. By the use of this "process" screen, personal error is almost entirely eliminated.

It is shown, further, that the intensities determined by the above method can be expressed in terms of the intensity of the continuous black body radiation from the positive crater of the carbon arc.

The results obtained show that the distribution of intensity in

the lines belonging to a particular series varies with the conditions of discharge. Under conditions in which there is a transfer of energy from the longer to the shorter wave-lengths in a given series it is found that the associated series, in particular the diffuse series, are relatively enhanced at the expense of the principal series. It has also been found that the distribution of intensity observed in certain celestial spectra can be approximately reproduced in the laboratory.

The question of the relative behaviour of hydrogen and helium cannot be satisfactorily discussed until the nature of the Balmer series is established. According to Sommerfeld, the Balmer series represents effectively a supposition of diffuse, sharp, and principal series, but the authors' measurements of the separation of the doublets constituting the lines H_α and H_β afford no support for this view. The measured separations are 0·132 Å. and 0·033 Å. respectively, and it is pointed out that these values are consistent with the hypothesis that the lines in question are principal series lines. The separation in the case of H_α is in precise agreement with the value deduced by Buisson and Fabry. H. M. D.

Wave-lengths of the Stronger Lines in the Helium Spectrum. PAUL W. MERRILL (*Chem. News*, 1917, **116**, 130—133). —The wave-lengths of twenty-one of the stronger helium lines have been measured by using a Fabry-Perot interferometer. In nine cases the wave-lengths were compared directly with that of the standard cadmium line by photographing the two spectra simultaneously on the same plate. The estimated error in the measurements is less than 0·003 Å.

In regard to the representation of the helium series by a three-constant formula of the type $n=A-B/m^2-C/m^3$, in which n is the frequency, m a series of successive integers, and A, B, and C are constants, it is shown that the formula based on the measurements of lines for which $m=3$, 4, and 5 in each of the six series, does not reproduce accurately the frequency of even the next number ($m=6$) in any one of the series. In every instance the divergence between the observed and calculated values is greater than the error of experiment, whilst the residuals show a fairly smooth and converging increase towards the terms of higher order. H. M. D.

The First Electron Ring of the Atoms. P. DEBYE (*Physikal. Zeitsch.*, 1917, **18**, 276—284).—According to Bohr's theory, the K series of lines in the high frequency spectra is attributable to the innermost ring of electrons. The frequencies of the α lines of the K series in the spectra of the elements between sodium (atomic number 11) and neodymium (atomic number 60) are considered in reference to Sommerfeld's formula, and it is suggested that the applicability of this formula to the K series of lines can be satisfactorily explained on the assumption that the innermost ring of electrons in the atoms of all elements, with the exception of those of low atomic number, consists of three electrons.

H. M. D.

Absorption Spectra and Chemical Constitution of Organic Compounds. J. J. DOBBIE, E. C. C. BALY, and A. W. STEWART (*Brit. Assoc. Rep.*, 1916, 131—186).—An alphabetical list of all organic compounds the absorption spectra of which have been measured in the infra-red, visible, and ultra-violet regions of the spectrum, with references in each case. C. H. D.

The Chromophore Function. I. LIFSCHITZ (*Zeitsch. wiss. Photochem.*, 1916, **16**, 140—152. Compare this vol., ii, 62).—As a qualitative method for the investigation of the absorption, the Hartley-Baly method has been found to be very convenient, and it is shown that the observations made according to this mode of procedure may be utilised in the determination of the magnitude of the extinction-coefficient for light of different wave-lengths. The values obtained in this way are found to be in satisfactory agreement with the extinction-coefficients afforded by direct measurement.

The question of the possibility of calculating the absorption of a compound from constants characteristic of certain groups is discussed, and theoretical arguments are advanced against the view that this is feasible. H. M. D.

The Influence of Constitution on the Rotation of Optically Active Substances. IX. Absorption Spectra of some Compounds with "Relatively Abnormal" Rotation-Dispersion. H. RUPE and L. SILBERSTROM (*Annalen*, 1917, **414**, 99—111).—A suggestion put forward by Tschugaev (A., 1911, ii, 450) to the effect that anomalous rotation-dispersion is connected with selective absorption in the ultra-violet, in the neighbourhood of the visible spectrum, has been investigated in the case of some dienes obtained by the action of Grignard agents on citronellaldehyde, some menthyl and myrtenyl esters, and some camphor derivatives. No such connexion has been established in these cases, for no substance examined has a selective absorption, although many have "relatively abnormal" rotation-dispersion (compare A., 1915, ii, 717; A., 1914, i, 131), verging in the case of diphenylmethylenecamphor into the really anomalous. Curves connecting wave-lengths with the logarithms of the layer thicknesses in millimetres are reproduced.

The preparation of diphenylmethylenecamphor and diphenylcamphorylmethane is described (compare Haller and Bauer, A., 1906, i, 441). The present authors find somewhat different constants for these compounds: diphenylmethylenecamphor has m. p. 113·5°, $[\alpha]_D^{20}$ +242·99°, in 10% benzene solution (Haller and Bauer found m. p. 113·5°, $[\alpha]_D$ +287° in alcohol); diphenylcamphorylmethane has b. p. 225°/12 mm., m. p. 135·5—136·5°, $[\alpha]_D^{20}$ +19·87°, 19·32°, in 10% benzene solution (Haller and Bauer found m. p. 106—107°, and $[\alpha]_D$ varying from +40°29′ to 80°10′). It is proposed, therefore, to investigate compounds of these types more thoroughly. J. C. W.

Production of Light at Low Temperatures by Catalysis with Metal and Metallic Oxide Hydrosols. B. C. Goss (*J. Biol. Chem.*, 1917, **31**, 271—279).—When a solution of pyrogallol is mixed with hydrogen peroxide in the presence of certain colloidal metal and metallic oxide sols, oxidation occurs rapidly with the production of white light. Visible light is produced in the presence of concentrations of colloidal platinum as low as 1 part in 250,000, whilst with higher concentrations similar effects are observed even when the temperature of the solutions is below zero. Gelatin, egg-albumin, and other protective colloids inhibit the production of light, whilst potassium stearate and amyl alcohol markedly increase it. The action of the colloidal metal is similar to that of the plant oxydases (Harvey, *Amer. J. Physiol.*, 1916, **41**, 454), except that in the former case the catalyst is not destroyed. The catalysis is apparently not due entirely to the high degree of dispersion of the metal or oxide and the consequent large specific surface, but is also dependent on the ability of the metal to form unstable compounds with oxygen. The phenomenon closely resembles that observed in luminous organisms. H. W. B.

Bioluminescence. VIII. Mechanism of the Production of Light during the Oxidation of Pyrogallol. E. Newton Harvey (*J. Biol. Chem.*, 1917, **31**, 311—336. Compare this vol., i, 365, and Goss, preceding abstract).—In addition to the substances already recorded, chromates, dichromates, hypochlorites, hypobromites, hypoiodites, chromium and iron salts, colloidal silver, oxides of manganese, metallic silver, and silver oxide all produce light when mixed under certain conditions with pyrogallol and hydrogen peroxide. Ferrocyanide solutions only give a bright light with pyrogallol and hydrogen peroxide after exposure to sunlight and air, due, apparently, to the formation by photochemical action of a substance in the ferrocyanide which is able to effect the rapid transfer of oxygen from the hydrogen peroxide to the pyrogallol. Perborates, persulphates, sodium and barium peroxides may replace hydrogen peroxide without inhibition of light production in the presence of some of the above oxidising agents, but not of others. The presence of a peroxide is not always absolutely essential; pyrogallol mixed with sodium hypochlorite or hypobromite, with ozone, or with acid (but not neutral or alkaline) permanganate, is rapidly oxidised with the evolution of visible light. Alkali sometimes favours luminescent oxidation and sometimes inhibits it; the action of acid also varies according to the oxidising agent present.

The effects of variation of the concentration and of temperature on light production during the oxidation of pyrogallol by potassium ferrocyanide in the presence of hydrogen peroxide have been ascertained. There is an optimum concentration of pyrogallol and of ferrocyanide at which the intensity of the light produced is a maximum. Increase of temperature also increases the brightness of the light up to an optimum temperature; then a decrease occurs. The greater the concentration of the reacting solutions, the higher

the optimum temperature for maximum light production. Light is also produced when the oxidation of the pyrogallol occurs in 50% alcohol or acetone. H. W. B.

Interference Effects of Irregularly Orientated Particles in Röntgen Light. III. The Constitution of Graphite and Amorphous Carbon. P. DEBYE and P. SCHERRER (*Physikal. Zeitsch.*, 1917, **18**, 291—301).—The methods introduced by von Laue and by Bragg for the investigation of crystal structure require well-formed crystals and also a knowledge of the system to which the crystals under examination belong. In the method which has been described by the authors (compare also *Physikal. Zeitsch.*, 1916, **17**, 277), it is unnecessary to have any information relative to the crystallographic system, and the investigation of the structure can be effected on crystals of microscopic or even sub-microscopic dimensions. The interference figures are obtained by pressing the crystalline powder to form a small rod, which is placed in the axis of a cylindrically arranged sensitive film and subjected to the influence of monochromatic Röntgen radiation, when characteristic curves are produced on the film as a result of the interference phenomena which are conditioned by the characteristic structure of the minute crystals.

This method has been applied in the investigation of the structure of graphite and amorphous carbon. The crystallographic data for graphite in the literature are quite contradictory, and the fact that the system to which graphite belongs has not previously been fixed with certainty is entirely due to the lack of well-formed crystals of sufficient size. The interference curves show clearly that graphite is trigonal, and the arrangement of the carbon atoms follows from the nature of these curves.

By subjecting amorphous carbon to examination in similar manner, interference figures are obtained which suggest that this amorphous variety is identical in structure with graphite, and that it only differs from graphite by its greater degree of subdivision.

The authors thus conclude that diamond and graphite are the only two known modifications of carbon. In the former the carbon valencies are arranged tetrahedrally, whilst in graphite the carbon atom appears to have its three principal valencies in one plane inclined to another at 120°, whilst the fourth valency (secondary) is disposed at right angles to this plane. This is said to correspond with the difference in chemical behaviour. H. M. D.

Separation of Isotopes. FREDERICK SODDY (*J. Amer. Chem. Soc.*, 1917, **39**, 1614—1615).—A criticism of a recent statement by Richards and Hall (this vol., ii, 230) of the existing position of the evidence on which is based the view that isotopes are not separable by chemical means. This view is not to be judged by a particular line of evidence, whether this is the proof that each radio-element has an isotope to which it is more closely allied than to any of the other elements, or the non-separability by the frequent repetition of the same operation on the same pair or by the

application of all the available methods to the same pair, but by the agreement of the results which are afforded by all three methods of investigation. H. M. D.

Periodicity among the Radioactive Elements. NORRIS FOLGER HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1616—1619).—By reference to the elements with atomic numbers 81 to 92, it is pointed out that the number of known isotopes in a pleiad and the character of the predominant radiation show a periodic variation of the type to be expected on the hypothesis that the atoms are built up from hydrogen and helium. This periodicity of two has already been noted by Harkins in the variation in the abundance and the atomic weight of the lighter elements and in the stability of the heavier elements. In so far as isotopic complexity and predominant radiation are concerned, it appears that the isotopes of even-numbered elements are more numerous than those of odd-numbered elements. The former show a well-marked tendency to undergo disintegration with the emission of α-rays rather than β-rays. This accords with the hypothesis that even-numbered elements belong to the helium system. H. M. D.

The Relative Electrode Potentials of Tin and Lead determined by Equilibrium Measurements with their Perchlorates. ARTHUR A. NOYES and KEBE TOABE (*J. Amer. Chem. Soc.*, 1917, **39**, 1537—1545).—The equilibrium in the system $Sn(solid) + Pb^{\cdot\cdot} = Pb(solid) + Sn^{\cdot\cdot}$ has been examined in a series of experiments in which metallic tin and lead, in the form of very fine shavings, were brought into contact with solutions of the corresponding perchlorates, the mixtures being rotated in stoppered bottles for ten to twenty days at 25° until a condition of equilibrium was attained. The perchlorates of both metals are soluble and are probably normally ionised. For these and other reasons, the perchlorates probably afford more satisfactory material for the investigation of the equilibrium in question than most other salts.

The measurements gave 2·98 as the mean value of the equilibrium ratio Sn/Pb. In previous measurements with chloride solutions, Sackur (A., 1904, ii, 336) found 3·34 to 3·45 for this ratio. The smallness of the difference between the two values suggests that the formation of complexes in the chloride solutions is not very considerable.

Assuming that the tin and lead perchlorates are equally ionised, the value 2·98 represents also the ratio $Sn^{\cdot\cdot}/Pb^{\cdot\cdot}$, and from this the difference between the normal electrode potentials of tin and lead is found to be $E_{Sn} - E_{Pb} = +0·0140 \pm 0·0001$ volt. According to data in the literature, the normal potential of lead referred to the hydrogen electrode is $+0·132$ volt, and therefore the normal potential of tin is $+0·146$ volt. It should be noted that the positive sign, which is given to these electrode potentials, is opposite to that which is commonly employed. H. M. D.

Electromotive Behaviour of Lead. PAUL GÜNTHER (*Zeitsch. Elektrochem.*, 1917, **23**, 197—199).—It is shown that lead electrodes capable of yielding sharp potential measurements of lead may be prepared by electrolytically depositing lead on a platinum wire from a 0·1005*N*-solution by a current of 1—2 milliamperes. With this electrode, the combinations $Pb|PbCl_2(sat.)||AgCl|Ag$ and $Pb|PbCl_2(sat.)||Hg_2Cl_2|Hg$ were measured. From the results, the heat change of the reaction $Pb + 2AgCl = PbCl_2 + 2Ag$ is found to be $U_0 = 12,195$ cal., and the heat of formation of lead chloride is 85,400 cal. The heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ is $U_0 = 10,870$ cal., and the heat of formation of lead chloride 85,380 cal. A number of heats of formation for various lead salts has been calculated from the present measurements. The following values are given: $PbBr_2$, 67,100 cal.; PbI_2, 42,400 cal.; $Pb(NO_3)_2$, 108,100 cal.; $PbSO_4$, 218,800 cal.; $PbCO_3$, 169,500 cal.; PbO, 52,900 cal.; PbS, 20,900 cal.; PbSe, 18,400 cal.; PbTe, 14,000 cal. J. F. S.

The Theory of Electrolytic Ions. VII. Determination of the Constitution of Complex Salts by Mobility and Conductivity. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **95**, 340—352. Compare this vol., ii, 14).—The constitution of complex multivalent salts cannot be determined from determinations of the transport numbers or of the conductivity alone, but may be so from a comparison of transport number and conductivity. These relations are discussed mathematically, with application to the complex salts of cobalt. C. H. D.

Chemical Reactions in Anisotropic Liquids. IV. THE. SVEDBERG. (*Kolloid Zeitsch*, 1917, **21**, 19—21. Compare this vol. ii, 249).—The influence of a magnetic field on the rate of change of the electrical conductivity of solutions of pyrogallol and picric acid in *p*-azoxyphenetole has been investigated under more favourable conditions, rendered possible by the use of a large and powerful electromagnet.

Under the influence of the field, the rate of increase of the conductivity becomes smaller, but the ratio between the rates with and without the magnetic action is independent of the nature of the solute, which is supposed to act as a catalyst, and also of the magnitude of the absolute velocity of reaction as measured by the rate of change of the conductivity. Between 9000 and 3500 gauss, this ratio is also independent of the strength of the field, but has a distinctly greater value for a field of 500 gauss. With rise of temperature, the ratio increases and becomes equal to unity at the clearing temperature. H. M. D.

Homogeneous Equilibrium and Additivity of Internal Atomic Heats ($C_v - 3/2\,R$) in Ideal Gases. MAX TRAUTZ (*Zeitsch anorg. Chem.*, 1916, **95**, 79—104. Compare A., 1916, ii, 304, 422). —The rule of additivity of internal atomic heats holds good exactly

or very approximately in the great majority of cases. Such deviations as are found are irregular. The molecular composition of a gaseous mixture is more uncertain the higher the temperature. The rule of additivity is tested by means of a large number of tables. C. H. D.

Molecular Heat of Zinc Dimethyl Vapour. An Example of the Additive Nature of $C_v - 3/2R$. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1917, **23**, 206—212).—The contradiction, met with between the dissociation of iodine and bromine, with respect to the additive character of the atomic heat, is discussed. It is shown that the integration constant of the bromine dissociation equilibrium differs by 2·7 units from that derived from the additive nature of $C_v - 3/2R$. This example shows that even in the case of a fundamentally divergent example a very considerable approximation of the equilibrium may be achieved from the additive nature of $C_v - 3/2R$. The molecular heat of zinc dimethyl may be calculated to 12·6 on the basis of strict additivity, whereas the experimentally determined value lies between 12 and 13. The molecular heat of carbon dioxide at the ordinary temperature is found by Kundt's method to be 8·56, a value in agreement with previous measurements and diverging from the value calculated on the basis of additivity. From these results it is stated that the additivity of $C_v - 3/2R$ is extremely good in the case of gases of similar character, but is never absolute. J. F. S.

Thermodynamic Contents of Ammonia. I. The Heat Capacity of Liquid Ammonia. FREDERICK G. KEYES and HENRY A. BABCOCK (*J. Amer. Chem. Soc.*, 1917, **39**, 1524—1537).—Measurements of the specific heat of liquid ammonia have been made by a mixture method in which the heat capacity of the ammonia is compared directly with that of water. The comparison is effected by the use of two bombs of the same weight, shape, and heat capacity, the weight of water in the water bomb being adjusted by trial experiments until its heat capacity is identical with that of the ammonia in the ammonia bomb. By this mode of procedure, the water equivalent of the calorimeter is eliminated, and the uncertainty respecting the temperature of the bomb at the instant it passes into the calorimeter is removed by an exactly reproducible method of rapidly transferring the bomb from the thermostat to the calorimeter. A small correction is, however, required for radiation, because of the fact that the rates of equalisation of the temperature in the calorimeter are different for the two substances concerned.

In terms of the specific heat data for water recorded by Bousfield, the measurements give 1·152 for the mean specific heat of liquid ammonia between 0° and 20°, and 1·172 between 20° and 50°. These specific heat values are expressed in 15° calories. Assuming that the true specific heat is a linear function of the temperature, it may be represented by the equation $c = 1{\cdot}144 + 0{\cdot}0008t$. H. M. D.

Use of Shukov's Apparatus for Molecular Weight Determinations. Ed. Graefe (*Zeitsch. angew. Chem.*, 1917, **30**, i, 44. Compare A., 1916, ii, 123).—The author has used a Shukov apparatus for some years in the determination of molecular weights by the depression of the melting-point method, and has found the apparatus to be quite suitable for the purpose. A vacuum jacket is not essential if the apparatus has double walls. Stearic acid is a useful solvent in many cases. W. P. S.

The Melting Points of Homologous Series. G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 172—176; from *Chem. Zentr.*, 1917, i, 1070).—Aliphatic monocarboxylic acids with an even number of carbon atoms have higher m. p.'s than the preceding or succeeding acids with an odd number of carbon atoms. According to the author, this regularity may be due to the fact that the former occur in two stable, crystalline forms, whilst only one stable form of the latter is known. The equilibrium diagrams show the probability of this hypothesis at any rate for the first two members of the series, formic and acetic acids. H. W.

The Guldberg and Trouton-Nernst Rules in Homologous Series of Compounds. W. Herz (*Zeitsch. anorg. Chem.*, 1916, **95**, 253—256. Compare A., 1916, ii, 311).—The ratio of the absolute boiling point to the critical temperature, which according to Guldberg's rule should be constant and equal to two-thirds, is shown to increase in homologous series with the number of carbon atoms.

Trouton's rule is found to give irregular results when tested in the same way, whilst the values corresponding with Nernst's formula increase with increasing carbon. C. H. D.

Vapour Pressures in the System: Carbon Disulphide–Methyl Alcohol. E. H. Büchner and Ada Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1232—1242).—When the vapour, which is in equilibrium with the conjugate solutions formed by a pair of partly miscible liquids, is intermediate in composition with respect to that of the two liquid solutions, it has been assumed that when the temperature reaches the critical solution temperature, the composition of the vapour will be the same as that of the critical solution. Although this view has been shown to be untenable on theoretical grounds, there is no experimental evidence which bears directly on the question. In these circumstances, the authors have investigated the conditions of equilibrium in the system carbon disulphide–methyl alcohol in the neighbourhood of the critical solution temperature 37·3°. The vapour pressures of various mixtures of the two substances at different temperatures are recorded in tables, and the composition of the vapour in equilibrium with the conjugate solutions at certain temperatures is also shown.

From the observations, it is not possible to say whether the composition of the vapour in this particular system remains inter-

mediate to that of the two liquids right up to the critical solution temperature, but this appears to be the case at all temperatures below 35·2°, which is only 2° below the critical temperature.

H. M. D.

Experimental Manipulation. The Manipulation of Small Quantities of Volatile Substances. II. ALFRED STOCK (*Ber.*, 1917, **50**, 989—1008. Compare A., 1914, ii, 171).—A complicated apparatus is described and figured, which is designed for the fractional distillation and determination of the physical constants of small quantities of volatile substances. It embodies all the features of the apparatus designed from time to time by the author in his work on boron, silicon, and carbon compounds (compare A., 1915, ii, 339; this vol., ii, 192, 308).

J. C. W.

Determination of Gas Density. J. D. EDWARDS (*J. Ind. Eng. Chem.*, 1917, **9**, 790—792).—A specific gravity balance is mounted in a water-jacketed gas chamber, which is closed by screw-caps and provided with a gas inlet, mercury gauge, and a needle-valve. The balance beam carries at one end a closed globe and at the other a pair of adjustable counterweights. The gas chamber is first filled with air and the pressure adjusted by means of the needle-valve until the beam just balances at a predetermined point. The operation is then repeated with the gas under examination. The specific gravity of the gas is the ratio of the total pressure (gauge plus atmospheric pressure) at which the beam balances in air to the total pressure at which it balances in the gas.

W. P. S.

Vacuum-jacketed Pyknometer for Liquids. FRANK HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1319—1320).—A pyknometer of the type described by Davis and Pratt is modified by the addition of a vacuum jacket. In use the inner portion is washed out two or three times with the liquid the density of which is required, after this liquid has been brought to the desired temperature. The pyknometer fitted in this way does not require to be immersed in a constant temperature bath, and the adjustment of the level in the capillary tube can be made at once.

H. M. D.

Influence of Unsaturation on the Molecular Volumes of Solid Compounds. GERVAISE LE BAS (*Chem. News*, 1917, **116**, 97—98).—Examples are given to show that the ethenoid linking of an unsaturated compound causes a contraction which has approximately the same value for a large number of aromatic compounds.

H. M. D.

The Surface Tension of Stereoisomeric Compounds. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **82**, 1—8).—The surface tension of solutions of certain stereoisomerides differed from one another when measured by stalagmometric methods. This was found to be the case with the limonenes (*d*- and *l*-), pinenes (*d*- and *l*-), and mandelic acids (*l*- and *i*-).

S. B. S.

Viscosity of Solutions. SVANTE ARRHENIUS (*Bio-Chem. J.*, 1917, **11**, 112—133).—A discussion of recent measurements of the viscosity of solutions and pseudo-solutions, with special reference to Einstein's formula and the empirical logarithmic formula suggested by the author (A., 1888, 336). This leads to the conclusion that Einstein's formula, as applied to colloidal solutions, represents a limiting law which is not in accord with the behaviour of actual solutions, in that for these the viscosity increases with the concentration more rapidly than the law demands. The deviations are attributable to the Brownian motion, to the non-spherical form of the colloidal or suspended particles, and to the formation of aggregates by combination with the solvent. The logarithmic formula has a much larger range of validity, and is applicable to true as well as to pseudo-solutions. Deviations from the logarithmic formula $\log \eta = \theta c$, in which θ is a constant, are brought about by dissociation of the solvent or solute molecules or by association between molecules of the solvent and the solute. Hatschek's objections to the logarithmic formula are criticised adversely. H. M. D.

Adsorption of Sulphuric Acid by Ferric Hydroxide and Formation of Colloidal Sulphur from Sulphides. E. DITTLER (*Kolloid Zeitsch.*, 1917, **21**, 27—28).—Experimental results are recorded which show that sulphuric acid is adsorbed by ferric hydroxide to such an extent that errors may be introduced in the estimation of sulphur in pyrites by Lunge's method.

By the action of steam on pyrites and marcasite for prolonged periods, it has been found that small quantities of colloidal sulphur are produced. It is suggested that native sulphur may in some cases have been formed by a similar action. H. M. D.

Adsorption by Soils. J. E. HARRIS (*J. Physical Chem.*, 1917, **23**, 454—473).—Finely divided dry soil or kaolin has been treated with a number of salt solutions of various concentrations, and the adsorption of the various cations and anions determined. Under this treatment it is shown that the cation adsorption follows very closely the adsorption isotherm represented by the equation $x/m = ac^{1/n}$, indicating that the action is one of pure adsorption and not of double decomposition. The adsorption differs with different salts, the order of adsorption tendency for the cations being $Al^{\cdot\cdot\cdot}$, $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Na^{\cdot}$, the adsorption values for calcium, manganese, and magnesium being almost alike. In the above series it is clear that, with the exception of potassium, the metals follow the order of their valency, and metals of the same valency give practically the same adsorption value. It was found that a soil which had adsorbed large quantities of potassium would give up part of this when treated with various salt solutions. In the case of the solutions used, it was found that they follow the order $AlCl_3$, NH_4Cl, $MnCl_2$, $CaCl_2$, $CaSO_4$, $MgCl_2$, NaCl, $CaCO_3$ with respect to their ability to remove adsorbed potassium. When a soil was treated with a solution of a mixture of salts, it

was found that the amount of each ion adsorbed was reduced by the presence of the other. The total number of equivalents adsorbed from the mixture was, however, greater than that from either salt alone. J. F. S.

Semipermeable Membranes and Negative Adsorption. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 441—453).—A theoretical paper in which semi-permeability and negative adsorption in its connexion with osmosis are discussed. It is shown that osmotic phenomena are exhibited by a porous diaphragm provided that there is a marked negative adsorption and that the diameter of the pores is so small that the adsorbed films practically fill the whole of the pores. A porous diaphragm will act as a semipermeable membrane when there is no measurable adsorption of the solute and when the adsorbed films fill the pores completely. In the usual case of a semipermeable diaphragm there is no porous wall, and the semipermeability is due to the fact that the solvent dissolves in the diaphragm, whilst the solute does not do so, to an appreciable extent, under the usual experimental conditions. A liquid is not to be considered as a porous substance, and solubility does not depend on porosity. J. F. S.

Capillary Phenomena and Supercooling. S. LAWRENCE BIGELOW and EDWARD A. RYKENBOER (*J. Physical Chem.*, 1917, **23**, 474—512).—The temperature of solidification of sulphur, aceto-*o*-toluidide, *β*-naphthol, acetanilide, oxalic acid, and benzoic acid has been determined in tubes varying in internal diameter from 4·8 mm. to 0·132 mm., with the object of ascertaining whether any relationship could be observed between the diameter of the tube and the amount of supercooling. The measurements were made in a rather complicated sulphuric acid bath fitted with an arrangement for withdrawing the hot acid and leading in cold acid. It is shown that, whilst a mathematical connexion between the diameter of the tube and the amount of supercooling could not be found, a great degree of supercooling is observed in the narrower tubes. The authors offer a theory to explain the phenomena observed. It is shown that the nature of the material of the tube has little, if any, effect on the amount of supercooling, and that small changes of surface tension and changes in the rate of cooling have no influence on the amount of supercooling. In the case of sulphur, it is shown that the amount of supercooling depends on the temperature to which the substance was previously heated. J. F. S.

The Partial Separation by Thermal Diffusion of Gases of equal Molecular Weight. S. CHAPMAN (*Phil. Mag.*, 1917, [vi], **34**, 146—151).—Theoretical reasoning leads to the conclusion that a temperature gradient in a mixture of two gases is sufficient to produce diffusion, independently of any non-uniformity of composition or of the action of external forces. It is now shown that "thermal diffusion" offers a means of partly separating two gases of equal molecular weight provided that the diameters of the two

kinds of molecules or the laws of their interaction are not identical. When the diameters are unequal, the larger molecules tend to pass towards the cooler regions. In its application, the method is limited by the approximate agreement of the diameters of many molecules of the same mass. H. M. D.

The Theory of Solution. E. J. HARTUNG (*Trans. Faraday Soc.*, 1916, **12**, 66—84).—The density, heat capacity, and heat change on mixing have been determined for a series of mixtures of selected pairs of liquids. The two liquids are introduced into the thin copper calorimeter, internally silvered, by means of weight pipettes, and stirred with a glass disk stirrer. The deviations of the observed properties from a simple mixture law are plotted by Denison's method (A., 1913, ii, 30), and the solvate explanation is adopted, although the variations in the curves suggest that two or more solvates may be present, and a quantitative verification is not possible. Nitrobenzene and ethyl ether exhibit a very small heat change on mixing, and the heat capacity scarcely deviates from the mixture law, although the contraction on mixing is considerable. The deviation curve is unsymmetrical. For aniline and ethyl ether, the curves for all three properties are similar and unsymmetrical, and do not correspond with any single solvate. For aniline and methyl alcohol, the deviation curves for contraction and heat capacity both pass through a maximum, but are otherwise dissimilar, whilst the heat change curve has both a maximum and a minimum. Aniline and carbon tetrachloride give a large absorption of heat on mixing, and the curves are not quite symmetrical. C. H. D.

Influence of Salts on Solubility. H. VON EULER AND OLOF SVANBERG (*Zeitsch. Elektrochem.*, 1917, **23**, 192—197).—The influence of a number of electrolytes on the solubility of certain non-electrolytes in water has been determined, together with the change in surface tension of the solutions. With regard to the effect of sodium salts of aliphatic acids and inorganic acids, it is shown that the solubility of aniline, nitrobenzene, and ethyl ether in water is reduced, but in the case of sodium salts of aromatic acids, the solubility is increased. The authors show that whilst there is a certain parallelism between the surface tension and the solubility, yet no definite relationship between the two can be formulated. The authors attribute the difficulty of bringing the solubility influence into line with other ionic properties to the fact that the action in the present case is due to two superimposing influences, the one depending on the electrical charge of the ions, which changes the properties of the solution through electrostriction, and the other connected with the chemical nature of the ions, which often acts in the direction opposed to the former action. J. F. S.

Comparative Solubilities in Water, Pyridine, and in Aqueous Pyridine. WILLIAM M. DEHN. *J. Amer. Chem. Soc.*, 1917, **39**, 1399—1404).—The solubilities of some eighty-five miscel-

laneous compounds in water, pyridine, and a mixture of these in equimolecular proportions are tabulated, most of the data being new. The work was inspired by the discovery that helianthin is vastly more soluble in the mixture than in the pure liquids; 100 grams of water, pyridine, or mixture at 20—25° dissolve 0·02, 1·80, or 51·50 grams of helianthin respectively. It is found that certain other dyes, alkaloids, and nitrogen compounds (fifteen cases in all) share this property, whilst lactose, maltose, and raffinose are less soluble in the mixture than in either solvent. The results are briefly discussed in the light of the accepted views on solubility.

J. C. W.

The Relation between Chemical Constitution and Crystal Structure. P. Groth (*Zeitsch. Kryst. Min.*, 1915, **54**, 498—504).—It has been shown by von Eucken (*ibid.*, 410) that whilst the heat conductivity of crystals increases as the temperature falls, that of amorphous substances, such as glasses, decreases, and, further, that the conductivity of crystalline aggregates is less than that of individual crystals. It follows that heat conductivity is favoured by homogeneity, which in a crystal reaches a maximum at the absolute zero, when the atoms are at rest.

The structure of diamond crystals is in accordance with the quadrivalent character of the carbon atom, and from this it is argued that atoms in general must be regarded as anisotropic. Hence molecules are also anisotropic, in the sense that their properties vary in different directions. As the molecule increases in size, however, the anisotropic character becomes less apparent, and the externally directed forces which lead to crystallisation less strong. This explains why substances with very large molecules, such as the characteristic colloids, do not crystallise.

When a substance crystallises, whilst part of the molecular interatomic forces is transferred to neighbouring molecules, part of them persist in the crystal structure, as is shown by many instances of close relationship between chemical constitution and crystalline form. Such relationships are specially common among aromatic benzene derivatives, the benzene ring structure evidently exerting a determinative influence on the crystalline form. Among aliphatic compounds such relationships are far less common, but recent work has shown that if the chain structure be closed, as in the anhydrides of dibasic acids, to form a ring, the crystal structure is less subject to large variations (compare Stefl, this vol., i, 535). Recent determinations of the densities of maleic acid (1·609) and maleic anhydride (1·509) make it possible to determine the topic parameters of these compounds and to compare them with those of succinic acid and its anhydride:

Succinic acid, $\chi:\psi:\omega = 3{\cdot}413:5{\cdot}940:5{\cdot}097$; $\beta = 133°37'$.
Maleic acid, $\chi:\psi:\omega = 3{\cdot}977:5{\cdot}384:3{\cdot}783$; $\beta = 117°7'$.
Succinic anhydride, $\chi:\psi:\omega = 3{\cdot}711:6{\cdot}242:2{\cdot}873$; $\beta = 90°0'$.
Maleic anhydride, $\chi:\psi:\omega = 3{\cdot}814:5{\cdot}952:2{\cdot}854$; $\beta = 90°0'$.

The parameters of the anhydrides are much more closely related than those of the acids. Further investigations of aliphatic compounds with closed structures are suggested. E. H. R.

Crystal Structure. I. & II. A. SCHOENFLIES (*Zeitsch. Kryst. Min.*, 1915, **54**, 545—569; 1916, **55**, 321—352).—I. A theoretical paper, in which the author discusses the mathematical theory of crystal structure, with particular reference to the work of W. H. and W. L. Bragg. The relation between the space lattice and the homogeneous point system is carefully considered, and special emphasis is laid on the importance of the notion of the "Fundamentalbereich," or the space appropriated by each point in a point system. This conception is of considerable chemical importance. In a simple point system, each fundamental space contains generally one point, and every point is chemically and structurally similar. In a chemical compound, however, which is represented by a number of similar interpenetrating point systems, each fundamental space must contain one point of each point system, or, in other words, one of each kind of atom in the molecule. The atomic complex situated in the "Fundamentalbereich" corresponds, therefore, with a molecule.

Just as the "Fundamentalbereich" is subject to the coincidence movements appropriate to the symmetry of the system, that is, translations, rotations about an axis, and reflections in a plane, so the atomic complex is subject to these movements. It follows that the atomic complexes are not of necessity all similarly orientated in the structure, and may be present in enantiomorphous forms. If the structure contains complexes of only the one kind or the other, a right- or left-handed crystal results. It is to be noted that the symmetry or structure of the atomic complex situated in the fundamental space does not affect the symmetry of the structure as a whole. The latter is determined by the elements of symmetry which bring about the homogeneous repetition in space of the atomic complex. The complete system of atomic complexes produced by subjecting one of them to all the coincidence movements appropriate to the symmetry of the structure constitutes a group, which is contained in the fundamental space lattice.

It is shown that in certain cases the assumption of symmetrical atoms or points leads to higher symmetry than if the atoms be supposed asymmetric.

In a discussion on the structure of diamond, it is shown that the structure found by Bragg can be deduced by means of the general mathematical theory from a knowledge of the number of carbon atoms, 8, in the elementary cube. The same is true of zinc blende and potassium chloride.

II. Contains a further discussion of the properties of homogeneous point systems. The relation between such point systems and atomic complexes in a crystal structure is very fully discussed, and, in the light of the work of W. H. and W. L. Bragg, the structures of pyrites and quartz are deduced by means of the general mathematical theory of crystal structure. E. H. R.

Resistance Limits of Mixed Crystals and the Molecular Arrangement in Space Lattices. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 199—265; from *Chem. Zentr.*, 1917, i, 1056—1059).—If a reagent which only attacks the components of a mixed crystal is allowed to act on a series of binary mixed crystals, its action does not increase regularly with the content of the attackable components, but certain limits of resistance are observed. Up to a certain concentration, g_1, of attackable constituents, the mixed crystals, apart from the very small number of attackable molecules, are resistant at the surface to the reagent. If the content of attackable constituent is increased to g_2, this protective action entirely ceases and the reagent can completely dissolve or attack the susceptible component. With regard to their behaviour towards a reagent which only attacks one constituent, the series of mixed crystals can be divided into three portions: (1) the series containing from 100 to g_2 % of attackable constituent from which the latter can be completely withdrawn. (2) The series having from g_2 to g_1 % of attackable constituent, from which the reagent can only remove a portion of the latter. In the residues, the amount of attackable constituent diminishes with its increasing content in the original crystals. (3) The series having from g_1 to 0% of attackable constituent. In this case only so much of the latter is lost as is contained in the molecules on the surface of the crystal, which is therefore practically resistant to the reagent.

Three methods of determining the resistance limits are described; the first depends on a series of quantitative estimations, and requires considerable quantities of material, whilst the second avoids analytical determinations and can be performed on minute quantities of substance. In the third method, the *E.M.F.* of the alloy in solutions of its less noble constituent is determined against some other electrode. Mixed crystals from g_1 to pure noble metal show the potential of the latter; from the point g_1 the potential falls rapidly. The resistance limits of Cu–Au and Ag–Au mixed crystals have been thoroughly investigated for a variety of reagents, and the results are shown in a series of tables, for which the original must be consulted.

In general, the resistance limits of Cu–Au are similar to those of Ag–Au mixed crystals. The action of chlorides of the platinum metals and of gold chloride is, however, exceptional. In this case the affinity of silver for chlorine is evidenced, and, in consequence, solutions containing chlorides with eliminable chlorine atoms behave differently towards Ag–Au and Cu–Au alloys. When the mechanism of the reaction is similar, there appears to be no difference in the action of a reagent towards the two series. If the silver atoms in the mixed crystals are univalent, the same is true of the copper atoms. The action of oxygen from different oxidising agents on the Cu–Au alloy shows different resistance limits. The strongest oxidising agents are active at the limit $g_1=4/8$ mol. Cu, the less powerful (acid solution of V_2O_5) at $g_1=5/8$ mol. Cu, and the weaker at $g_1=6/8$ mol. Cu. The action of sulphur and selenium is analogous. The mercury ion shows an abnormal behaviour by

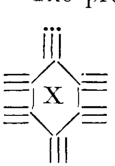
diffusing into the alloy without replacing an equivalent amount of copper. With solutions of silver salts and osmium chloride, strongly marked resistance limits occur at $g_1 = 7/8$ mol. Cu. Distinct resistance limits are not observed with mixed crystals of antimony and bismuth, but the rate of reaction decreases discontinuously with variation in the composition of the alloy.

The resistance limits of regular mixed crystals of gold lie at molecular fractions which are multiples of 1/8, and, with the hexagonal Sb–Bi mixed crystals the rate of action of different reagents alters abruptly at multiples of 1/6. A regularity exists here which, like of Law of Multiple Proportions, demands an atomistic explanation. In order to connect the resistance limits with the atomic structure, the disposition of the two kinds of molecules in the lattices must be known. If this is established, special properties of the reagent and of the active molecules of the mixed crystals can be deduced from the resistance limits. According to the properties of the crystals, an 8-point or 14-point lattice is involved. The resistance limits can be deduced from the molecular disposition which corresponds with the most thorough admixture of the two types of molecule which is compatible with the lattice symmetry.

H. W.

Topic Parameters in the Light of the Stereo-Hexite–Pentite Theory. W. Asch and D. Asch (*Zeitsch. Kryst. Min.*, 1915, **54**, 587—589).—The crystal structure of dihydrogen–potassium and dihydrogen–ammonium phosphates and arsenates were examined by Muthmann, who came to the conclusion, from a study of their topic parameters, that whereas replacement of potassium by ammonium or vice versâ produced an appreciable change in the dimensions of the structure in one direction only, the replacement of phosphorus by arsenic or vice versâ resulted in a general expansion or contraction in the structure in all directions.

The present authors formulate these salts as $3R_2O,6H_2O,3X_2O_5$, in accordance with the hexite–pentite theory, and propose the adjoined structural formula, in which the hexagon represents $3P_2O_5$ (or As_2O_5), the lines without dots represent OH-groups and those with dots OK-groups. The authors claim that the effect of isomorphous substitution of K for NH_4 or of P for As on a structure of this type will be in agreement with Muthmann's conclusions, which therefore lend support to the theory.



E. H. R.

The Influence of Temperature Variations on the Formation of Crystals. A. Schubnikov (*Zeitsch. Kryst. Min.*, 1914, **54**, 261—266).—Crystals left for some time in a saturated solution gradually lose their shape and tend to form a layer or disk on the bottom of the vessel. This phenomenon is attributed to alternate rise and fall of temperature. If the temperature rises, the crystal dissolves more at the top than at the bottom, whilst the solution tends to become more concentrated at the bottom, under the influ-

ence of gravity. Consequently, on cooling again, crystals are deposited more at the bottom.

The phenomenon of the growth of some faces of a crystal at the expense of others might be explained, if the process were an isothermal one, by the faces having different solubilities at one and the same temperature, so that at a particular temperature the solution might be under-saturated with respect to one face and supersaturated with respect to another. A more probable explanation, however, attributes the phenomenon to temperature variations. Experiments with potassium alum confirm this idea. For these experiments a special apparatus was designed, electrically controlled, by means of which a slow periodic variation of temperature was obtained. In the cube face of a crystal of alum a depression was made and was filled with saturated alum solution, the crystal being then placed in the apparatus for two days. At the end of this time the faces {100}, {110}, {111}, and {112} had appeared in the depression. Other experiments of a similar kind produced similar results.

The formation of concentric layers in the case of alum crystals is attributed to temperature variation and the enclosure of mother liquor. E. H. R.

The Relation between Rate of Growth and External Symmetry of Crystals. A. SCHUBNIKOV (*Zeitsch. Kryst. Min.*, 1914, **54**, 267—272).—In a previous paper (A., 1913, ii, 1031) it was shown that crystals deposited from a highly supersaturated solution are more symmetrical externally than those deposited from a less supersaturated solution. In the present paper, experiments with sodium chlorate are described, in which a crop of crystals is caused to be deposited from solutions of varying degrees of supersaturation. From seventy to eighty crystals of each crop were examined by determining the ratio of the lengths of the horizontal cube edges. The mean deviation of this ratio from unity was then determined by the method of least squares and compared with the degree of supersaturation. The results show clearly that the external symmetry of the crystals increases with the degree of supersaturation of the solution. E. H. R.

X-Ray Analysis of the Crystal Structure of Rutile and Cassiterite. C. M. WILLIAMS (*Proc. Roy. Soc.*, 1917, A, **93**, 418—427).—Well-formed crystals of the two isomorphous minerals were examined by means of the *X*-ray spectrometer, a special device being adopted in order to compensate for variations in the intensity of the source of the rays. The model of the crystal structure deduced from the experimental data differs essentially from that devised by Vegard for the same group of minerals, including zircon, the present author disagreeing with some of Vegard's experimental observations (A., 1916, ii, 405). The model now put forward possesses holohedral tetragonal symmetry, having a tetragonal screw axis and showing both {100} and {111} planes as cleavage planes. The enantiomorphous character of the struc-

ture may be correlated with the peculiar twinning of rutile and cassiterite.

The spectra obtained from corresponding faces of the two minerals are remarkably similar, although it might have been expected that in the case of rutile the greater relative mass of the oxygen atoms might modify the intensities of some of the orders of spectra. E. H. R.

The Purification of Salts by Clarification or by Fractional Crystallisation. E. RENGADE (*Compt. rend.*, 1917, **165**, 237—240).—When a mixture of two soluble salts having no common ion, such as ammonium nitrate and sodium chloride, is treated with a small quantity of water at the ordinary temperature, the sodium chloride disappears and is replaced by sodium nitrate and ammonium chloride. If the amount of water is increased progressively, the three salts, ammonium nitrate, sodium nitrate, and ammonium chloride dissolve simultaneously, the second in greater proportion than the third. The composition of the liquid remains constant until the whole of the sodium nitrate is dissolved. When this solution is removed and more water added, then the two ammonium salts dissolve in proportion to their simultaneous solubilities until the whole of the ammonium chloride is removed and the ammonium nitrate remains pure. Thus the purification requires two stages, and it is only necessary to determine by analysis the composition of the two corresponding saturated solutions to calculate the minimum amount of water necessary for the complete purification of one salt in a given mixture at a given temperature. W. G.

Orientation of Anisotropic Liquids on Crystals. F. GRANDJEAN (*Bull. Soc. franç. Min.*, 1916, **39**, 164—213; from *Chem. Zentr.*, 1917, ii, 40).—According to Mauguin (*Compt. rend.*, 1913, **156**, 1246), the drop of an anisotropic liquid is orientated in a definite manner when placed on a crystal face or cleavage fissure of muscovite. The author has independently been led to the following conclusions. Orientation of anisotropic liquids is caused by contact with crystals when it occurs at a surface of perfect cleavage, and the nature of such orientation is generally very simply related to the symmetry of the crystal. Observations were made with orpiment, blende, phlogopite, brucite, talc, pyrophyllite, rock salt, sylvine, and leadhillite, the anisotropic liquids employed consisting of azoxyphenetole, azoxyanisole, anisaldazine, ethyl azoxybenzoate, and ethyl azoxycinnamate. The differences observed during the use of the different crystals and liquids, as well as the methods of investigation, are described in the original. H. W.

The Theory of Gels as Systems of Two Liquid Phases. EMIL HATSCHEK (*Trans. Faraday Soc.*, 1916, **12**, 17—20).—On the assumption that gels consist of two liquid phases, one of which forms polyhedra and the other thin separating films, the apparent

elasticity on deformation must be due to the surface energy, any deformation increasing the internal surface. Calculations for the cube, rhombohedron, rhombic dodecahedron, and Kelvin's tetrakaidecahedron show that, the volume of the gel remaining constant, the stress increases until the structure has been extended to 2·52 times its original length, and then slowly decreases. Actual experimental curves, so far as they have been determined, fail to correspond in shape with that theoretically deduced. Rubber has been regarded as a gel, and its stress–elongation curve departs still more widely from the theoretical form. The two-liquid structure of gels is therefore improbable. C. H. D.

Determinations of the Compressibility of Disperse Systems. ARNE WESTGREN (*Zeitsch. anorg. Chem.*, 1916, **95**, 39—63).—The indirect method of determining the compressibility of colloids by measuring the number of particles in a geometrically limited volume at intervals of time (Svedberg and Inouye, A., 1911, ii, 703) is inaccurate, owing to the difficulty of delimiting the volume under observation, variations in the illumination and lack of uniformity in the colloidal particles being contributory causes of error. With high concentrations and fine hydrosols, the difficulty of counting the particles is also considerable. By diminishing the illumination and increasing the dimensions of the illuminating beam, more constant results are obtained. Observations of gold hydrosols of great uniformity (Zsigmondy, this vol., ii, 364) show that when the concentration is not greater than seventy-two particles per 1000 μ^3, the laws of Boyle and of Gay-Lussac hold good exactly. C. H. D.

Colour Change and Degree of Dispersity of Indicators. H. R. KRUYT and J. M. KOLTHOFF (*Kolloid Zeitsch.*, 1917, **21**, 22—26).—In view of the statement (Ostwald, A., 1912, ii, 439) that the colour changes of indicators are frequently accompanied by and may be attributed to changes in the degree of dispersity of the indicators, experiments have been made with a number of indicators, in which the colour of the solution, the Tyndall effect, and the ultramicroscopic appearance were examined in acid, neutral, and alkaline solutions. The results obtained show that there is no evidence to support the view that the degree of dispersity of the indicator is the determining factor in connexion with the colour change. H. M. D.

The Rhythmic Precipitation of Colloidal Mercury. HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1917, **39**, 1312—1314).—A method is described by which the author has obtained rhythmic precipitation of metallic mercury by the interaction of an aqueous solution of mercurous nitrate and an agar-agar jelly containing sodium formate. The agar-agar solution is drawn up into narrow glass tubes, where it sets to a jelly, and the tubes are then placed horizontally at the bottom of a dish containing a 2% solution of mercurous nitrate, slightly acidified, the dish being kept at a

temperature of about 50° for twelve hours. It is suggested that the formation of the banded deposit is due to the production of supersaturated solutions of colloidal mercury, and is cited as evidence in favour of the existence of supersaturation in colloidal solutions. H. M. D.

Formation of Layers in Suspensions of Soils and Clays. Their Explanation and their Application in the Investigation of Soils for Agricultural Purposes. PAUL EHRENBERG, ERNA HAHN, and OTTO NOLTE (*Kolloid Zeitsch.*, 1917, **21**, 1—19).—The literature relating to the formation of layers in suspensions is reviewed, and an account is given of new experiments which have been made with suspensions of ultramarine. Measurements of the concentration of the suspended substance and of the number of the particles in the more or less sharply differentiated layers indicate that the stratification is due to the circumstance that the size of the particles varies in such a way that the particles fall into discontinuous groups. In each of these groups the particles approximate in size to the mean value which is characteristic of the group; this is, moreover, appreciably different from the mean size of the particles belonging to the neighbouring groups. H. M. D.

Similarity of the Action of Salts on the Swelling of Animal Membranes and of Powdered Colloids. JACQUES LOEB (*J. Biol. Chem.*, 1917, **31**, 343—362).—Dried pig's bladder, freed from fat, when treated for a short time with a $M/8$-sodium chloride solution, swells considerably more when subsequently put into distilled water than it does if it remains permanently in the same salt solution or when it remains permanently in water without a previous salt treatment. The increased swelling appears to be due to an interaction between the salt and a constituent (probably protein) of the membrane, the resulting compound being capable of taking up more water than the untreated membrane. The subsequent swelling in water is apparently inhibited by an excess of salt, because the membrane remaining in salt solution does not swell so much as the membrane treated first with salt and then placed in water or very dilute salt solution. Salts with bivalent cations do not cause the increased swelling observed with sodium chloride; further, the addition of about 8 c.c. of $M/8$-calcium chloride solution to 100 c.c. of $M/8$-sodium chloride solution prevents the after-effect which a treatment with a pure $M/8$-sodium chloride solution produces. Similar effects are observed when the animal membrane is replaced by powdered gelatin or ovomucoid (and probably other powdered colloids), but not by solid blocks or sheets of gelatin, which suggests that the salt effects are due to an action on the surface of colloidal particles (fibres in the case of pig's bladder). This suggestion is supported by the fact that the effect of a previous treatment with the salt solution on the subsequent swelling of a given mass of powdered gelatin in water is greater when the size of the particles is smaller, and hence

the total internal surface greater. The mechanism of this swelling is apparently of a different nature from that observed in solid masses of gelatin under the influence of acid or alkali (compare Procter and Wilson, T., 1916, **109**, 307).

Experiments are described showing that the effect of salt on the subsequent rate of percolation of water through a layer of powdered gelatin varies inversely with the rate of swelling. A previous treatment with $M/8$-sodium chloride solution retards the percolation of water through the powdered gelatin, whilst a previous treatment with $M/8$-calcium chloride does not have any such effect. The addition of a small quantity of calcium chloride to the sodium chloride prevents the subsequent retardation of the rate of percolation of water, as it prevents the swelling.

The rate of percolation of water through finely powdered soil previously treated with various salt solutions is affected in the same manner as has been described in the case of powdered gelatin, but swelling of the particles of soil does not seem to take place.

H. W. B.

Ultramicroscopic Investigation of the Tanning Process in Jellies. W. MOELLER (*Kolloid Zeitsch.*, 1917, **20**, 257—270).—A further description is given of the conditions of formation of laminated structures in the action of aqueous solutions on jellies. The formation of an insoluble salt by the interaction of an electrolyte in the aqueous solution and a second electrolyte in the jelly is not an essential condition in the production of such structures. It has been found that an aqueous solution of silver nitrate when left in contact with a gelatin jelly containing no added electrolyte, gives rise to the formation of alternating layers. This cannot be attributed to the presence of small quantities of chlorides and phosphates in the jelly, for the same result is obtained when pure gelatin is used. The laminated structure would indeed seem to be produced when any ionisable salt diffuses into a jelly. The same heterogeneous structure results when gelatin jellies are subjected to the action of tanning solutions.

The laminated structures produced under specified conditions are illustrated by photographs and described in detail. It is considered that the ultra-microscope observations cannot be interpreted satisfactorily in terms of the hypotheses which have been previously put forward, and that the rhythmic lamination can only be accounted for in terms of the structure of the jelly. The author's view that gelatin consists of a fibrillated substance (α-gelatin), the spaces between the fibrils being filled by a structureless substance (β-gelatin), is made the basis of an explanation of the rhythmic effects which are the result of the diffusion processes which occur when jellies are brought into contact with solutions of salts. For details the original must be consulted.

H. M. D.

In-, Uni-, and Bi-variant Equilibria. XVI. & XVII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1196—1205, 1205—1217. Compare this vol., ii, 299, 411).—A further theoretical discussion of types of equilibrium, with

special reference to equilibria of n components in n phases at constant pressure. H. M. D.

Determination of the Heterogeneous Equilibrium of Water Vapour, particularly in the case of Iron and Tungsten. LOTHAR WÖHLER and W. PRAGER (*Zeitsch. Elektrochem.*, 1917, **23**, 199—206).—An apparatus is described, by which, through the use of a Sprengel mercury pump, a gas volume may be made to circulate at any given diminished pressure. This apparatus is used in the determination of the water-vapour equilibria in the case of iron and tungsten. The temperature curves of the reactions are shown to cut at 840°. The equilibrium relationship for tungsten at 940° is $K_{940^\circ}=1{\cdot}0$. Above 840°, iron is more noble than tungsten. The continuous action of water vapour on tungsten at high temperatures is attributed to the formation of a volatile tungsten oxide. J. F. S.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. The Interaction of Mixed Salt Solutions and Liquid Amalgams. IV. The Ionisation Relations of Sodium and Strontium Chlorides in Mixtures. G. McP. SMITH and S. A. BRALEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1545—1576).—In continuation of previous investigations (compare this vol., ii, 247), experiments have been made with a view to the elucidation of the ionisation relations in solutions containing sodium chloride and strontium chloride. The method of procedure has been previously described, and the data obtained afford directly information relative to the equilibrium between a liquid amalgam containing sodium and strontium and solutions of the chlorides of sodium and strontium. The mass-law constant,

$$C_c=[SrHg_m][NaCl]_c^2/[NaHg_m]^2[SrCl_2]_c,$$

in which $[NaHg_m]$ and $[SrHg_m]$ are the atomic fractions of the amalgamated metals and $[NaCl]$ and $[SrCl_2]$ the mol. fractions in the salt solution does not actually remain constant when the concentrations of the amalgam and of the salt solution are varied. It increases with the concentration of the amalgam, and for solutions which contain equivalent quantities of the two salts it decreases rapidly until the concentration reaches $0{\cdot}8N$, then more slowly, and attains a nearly constant value at $1{\cdot}6N$. The observed relations indicate that the sodium ion fraction increases with increasing salt concentration up to $1{\cdot}6N$, whilst there is a corresponding decrease in the strontium ion fraction. The value of C_c also depends on the temperature, and increases appreciably when the temperature is raised from 15° to 30°. H. M. D.

Tri-iodide and Tri-bromide Equilibria, especially in Cadmium Solutions. R. G. VAN NAME and W. G. BROWN (*Amer. J. Sci.*, 1917, [iv], **44**, 105—123).—The influence of the metal on the equilibrium in solutions containing free halogen and metallic haloids has been investigated by the distribution method. The

results obtained with strontium, nickel, zinc, and lanthanum iodides show that the equilibrium constant, $k=[\Sigma I][I_2]/[\Sigma I_3]$, has the same value as for the iodides of the alkali metals. On the other hand, for solutions of cadmium iodide the value of k is much larger and increases rapidly with increasing iodide concentration. Similar abnormality is shown by solutions which contain potassium iodide, together with cadmium or mercuric iodide. The corresponding constant for the bromine–bromide equilibrium shows abnormality of the same type in the case of cadmium bromide solutions and of solutions which contain potassium bromide together with cadmium or mercuric bromide. The abnormality is attributed to the presence of complex molecules or ions, and on the assumption that these do not combine with the halogen, it is shown that the measurement of the equilibrium constant k affords a method for the determination of the proportion of complex molecules and ions. From the results obtained with solutions which differ in respect of the iodine or bromine content, it is possible by extrapolation to determine the extent to which complex molecules are present in pure solutions of the metallic haloids. In this way it has been found, for instance, that 0·5, 0·25, 0·125, and 0·01 molar solutions of cadmium iodide contain respectively 6·0, 10·6, 16·8, and 55·0% of active iodide.

H. M. D.

The Effect of Pressure on the Equilibrium Constant of a Reaction in a Dilute Solution. A Simple Proof of the Expression. W. C. McC. Lewis (*Trans. Faraday Soc.*, 1917, **12**, 314—316).—The general expression $d \log K/dP =$ volume shrinkage$/RT$ has been obtained by Planck and others by means of the thermodynamic potential. A simpler deduction may be arrived at from the principle of maximum work.

C. H. D.

Equilibrium in Silicate Fusions and the Determination of the Melting Point of Calcium Silicate. C. Doelter (*Sitzungsber. k. Akad. Wiss. Wien, math-nat. Klasse*, 1911, **110**, 839—864; from *Zeitsch. Kryst. Min.*, 1914, **54**, 398).—The melting points of many silicates, determined by the thermal method, are too high owing to under-cooling or over-heating. With few exceptions (sodium, lithium, and lead silicates), there is no distinct melting point, the substance passing gradually from the crystalline, through a glassy, amorphous stage to the liquid condition over a certain temperature interval.

The thermal method being applicable only to quickly melting substances, the author employs (1) an optical method, using a hot microscope, whereby the melting process is observed directly, or (2) an approximate method, the finely powdered silicate being kept at the sintering temperature until the mass melts completely.

The influence of the size of the particles may amount to 100° or more. The rate of heating is important, and the velocity of melting or crystallising depends also on viscosity. It follows that the laws deduced from the phase rule and from thermodynamic principles apply to silicate fusions only in a modified form.

As a result of the non-observance of the above principles, large errors may arise. Whilst Day and Genossen found for wollastonite a melting point of 1260° and for calcium α-metasilicate 1512°, the author finds 1240—1320° and 1310—1380° respectively. A molecular change of wollastonite into the α-form was not observed, but it was noticed that above 1260° only the α-silicate separated. E. H. R.

Uniform Pressure, Deformation Pressure, and Rock Metamorphosis. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1916, **95**, 64—78. Compare A., 1915, ii, 242; Hasselblatt, A., 1916, ii, 299; Wegscheider, *ibid.*, 299).—The minerals in a primary (igneous or sedimentary) rock may either be in a state of true equilibrium or in one of almost complete inertia, owing to the low velocity of transformation. The number of components being usually at least nine, chemical changes almost always take place in the system when the external conditions are altered, plasticity and gliding playing, in the case of silicate rocks, no important part. The recrystallisations which take place in geological time are usually due to solution and re-deposition, especially with capillary water as the solvent. Non-uniform stress accelerates the change by, for example, increasing the solubility. The newly formed minerals are usually not those which result from magmatic fusion, but those which are formed by hydrothermal methods below 450°. This is illustrated by photomicrographs of chloritoid schists, the large porphyroblasts of chloritoid being surrounded by clear spaces, filled with quartz and chlorite. Actual flow of a solid phase into the capillary spaces probably does not take place in silicate rocks. It is not possible to apply definite formulæ on account of the indefiniteness of the stresses and of the fact that equilibrium is not attained. C. H. D.

Does the Law of Mass Action Regulate Diastatic Reactions? OCTAVE BAILLY (*Compt. rend.*, 1917, **165**, 248—250; *J. Pharm. Chim.*, 1917, [vii], **16**, 161—167).—Taking the results given by Bourquelot and Verdon (compare A., 1913, i, 542, 781) for the synthesis of β-methyl glucoside, the author has calculated the quantity of dextrose converted into glucoside from the equation $K = x(c+x)/(a-x)(b-x)$, where a, b, and c represent the molecules of methyl alcohol, dextrose, and water present at the commencement of the reaction, and x the molecules of dextrose converted. The first five values of x calculated agree exactly with the experimental values, and the last five show a difference of 2%. These results are considered to support an affirmative answer to the question. W. G.

Hydrolysis of Acetanilide. DAVID R. MERRILL and ELLIOT Q. ADAMS (*J. Amer. Chem. Soc.*, 1917, **39**, 1588—1598).—The hydrolysis of acetanilide in presence of hydrochloric acid proceeds at a rate which is proportional to the product of the concentrations of the unhydrolysed acetanilide and the hydrogen ion. The value

of the velocity coefficient at 100° is 8·4 when the hour is taken as the unit of time. The equilibrium constant for the reaction $NHPh\cdot COMe + H^{\cdot} + H_2O \rightleftharpoons NH_3^{\cdot}Ph + MeCO_2H$ is found by extrapolation to be $K=950$, from which the velocity coefficient for acetylation is found to be 0·0089 (time in hours). H. M. D.

Catalysis. Part III. Some Induced Reactions. NILRATAN DHAR (T., 1917, **111**, 690—706. Compare A., 1916, ii, 236).—Under ordinary conditions, and even on boiling, oxalic acid and other reducing agents do not reduce mercuric chloride to mercurous chloride. The author has investigated the action of various inductors on this and several similar reactions. The action of the oxidising agents, potassium persulphate, manganese dioxide, potassium nitrite, potassium permanganate, chromic acid, and nitric acid, on the reduction of mercuric chloride by oxalic acid has been studied. From the results, it is shown that the greater the concentration of the inductor, the greater is the amount of mercurous chloride obtained; this relation holds up to a certain limiting concentration of the inductor, after which an increase in the concentration of the inductor is accompanied in most cases by a decrease in the amount of mercurous chloride. The higher the temperature, the greater the amount of mercurous chloride formed. The greater the concentration of the actor, the greater the amount of reduction. Sulphuric acid hinders and manganese sulphate promotes the reaction. A similar series of experiments with some of the inductors has been carried out with tartaric acid, malic acid, malonic acid, glycollic acid, citric acid, hydrazine hydrochloride, and hydroxylamine hydrochloride, in each case with mercuric chloride. Similar results were obtained in all cases. A number of other reactions have been studied, including the reduction of copper chloride by organic acids in the presence of potassium permanganate as inductor; gold chloride by organic acids with various inductors; silver nitrate and organic acids in the presence of potassium permanganate as inductor, and sodium selenite and various reducing agents in the presence of potassium permanganate as inductor. A number of conductivity determinations have been carried out of some induced reactions. Experiments were made with oxalic acid and malonic acid as actors, mercuric and gold chlorides as acceptors, and potassium permanganate as inductor. The conductivity of the reaction mixture falls off very rapidly at first, and as soon as the reduction of the metallic salt begins, the conductivity again rises slowly. The results are discussed and tentative theories put forward to explain the results. J. F. S.

Catalysis. IV. Temperature-coefficients of Catalysed Reactions. NILRATAN DHAR (T., 1917, **111**, 707—762. See preceding abstract).—The author has studied the kinetics of the reduction of mercuric chloride by oxalic acid in the presence of catalysts, the oxidation of oxalic and formic acids by chromic acid, and the oxidation of oxalates and formates by iodine, mercuric

chloride, and silver nitrate. In the case of the oxidation of oxalic acid by chromic acid, it is shown that the reaction is unimolecular with regard to chromic acid and termolecular with regard to oxalic acid at 25°. The whole reaction is therefore quadrimolecular and may be represented by $H_2Cr_2O_7 + 3C_2H_2O_4 = Cr_2O_3 + 4H_2O + 6CO_2$, the neutralisation of the chromic oxide by oxalic acid being extremely rapid, and consequently not affecting the velocity of the reaction. It is shown that with increasing concentration of chromic acid, the velocity constant decreases, and this is attributed to the reaction between the oxalic acid and chromic oxide taking place with different velocities with changing concentration of oxalic acid. The temperature-coefficient of the velocity constant varies with temperature, the following values being found: between 25° and 30°, 1·95; between 50° and 60°, 1·72. In the presence of sulphuric acid of moderate concentrations, the velocity of the oxidation is increased, but a large excess of sulphuric acid retards the reaction. The temperature-coefficient is unaltered by the presence of sulphuric acid in moderate concentration, but in the presence of a large excess of sulphuric acid it is increased. In the presence of manganese sulphate as catalyst, the reaction is independent of the concentration of the chromic acid. The effects of molybdic acid, ammonium molybdate, and boric acid as catalysts of the oxidation of oxalic acid by chromic acid have also been studied. In the case of the oxidation of formic acid by chromic acid, the reaction is unimolecular with respect to chromic acid and termolecular with respect to formic acid, and may be represented $H_2Cr_2O_7 + 3H{\cdot}CO_2H = Cr_2O_3 + 6H_2O + 3CO_2$. No disturbing factors are observed in this case with change of concentration. The temperature-coefficient is 2·05, and is not influenced by change in concentration. The velocity of oxidation is much increased in the presence of sulphuric acid, and the temperature-coefficient is much reduced. Manganese sulphate retards this reaction, but has no influence on the temperature-coefficient. The influence of molybdic acid and manganese chloride as catalysts of this reaction has also been studied.

The oxidation of sodium formate by iodine is shown to be unimolecular with respect to both iodine and sodium formate; the whole reaction is therefore bimolecular, and may be represented $H{\cdot}CO_2Na + I_2 = HI + NaI + CO_2$. The reaction is retarded by iodine ions and has a temperature-coefficient of about 4, which is not changed by the negative catalyst, potassium iodide. Manganese sulphate retards the reaction, the velocity constant decreasing with increasing concentration of manganese sulphate.

The oxidation of sodium formate by mercuric chloride is unimolecular with regard to both substances, and consequently is a bimolecular reaction. The equation employed to represent the change would demand a termolecular reaction, which indicates that this reaction must occur in stages. This reaction has a temperature-coefficient of 3·63 and is retarded by manganese sulphate. This reaction is retarded by sodium acetate and the

chlorides of sodium, zinc, calcium, manganese, and strontium. In each case the temperature-coefficient is increased.

Silver nitrate is reduced by sodium formate according to a bimolecular reaction, of which the temperature-coefficient is 2·67 between 25° and 40° and 2·48 between 40° and 50°. Manganese sulphate acts as a negative catalyst in this reaction without changing the temperature-coefficient.

A number of experiments have been carried out both in the dark and in light with the object of ascertaining the mechanism of chemical change and temperature-coefficient. In the case of the oxidation of quinine sulphate by chromic acid, it is shown that in the dark the temperature-coefficient is 1·87, whereas in light the lower value 1·04 is obtained. The oxidation of potassium oxalate by iodine is shown to be unimolecular with regard to both substances; this reaction in the dark has a temperature-coefficient of 7·2 between 25° and 40°, 6·1 between 40° and 50°, and 5·4 between 50° and 60°; in diffused daylight, the reaction velocity is found to be less than in the dark and to have a temperature-coefficient of 3·36 between 25° and 50°. The oxidation of potassium oxalate by mercuric chloride in the dark at 99·6° is bimolecular, although it would appear from the equation to be termolecular The temperature-coefficient is 2·2 in the dark and 1·19 in the light. J. F. S.

A New Case of Reversible Catalysis: Direct Formation of Nitriles from Amines with the same Carbon Chain. PAUL SABATIER and G. GAUDION (*Compt. rend.*, 1917, **165**, 224—227).—In certain cases, the authors have been able to obtain the reverse of the catalytic hydrogenation of nitriles to amines by means of finely divided nickel (compare Sabatier and Senderens, A., 1905, i, 267). Thus, if the vapour of benzylamine is passed over nickel at 300—350°, benzonitrile is obtained. At the same time, the hydrogen produced in this process reduces more of the amine, giving toluene and ammonia, the whole course of the reaction being $3C_6H_5{\cdot}CH_2{\cdot}NH_2 = C_6H_5{\cdot}CN + 2C_6H_5{\cdot}CH_3 + 2NH_3$. Similarly, *iso*amylamine yields *iso*valeronitrile, *iso*pentane, and ammonia, the reaction being further complicated in this case, since a portion of the *iso*pentane is decomposed by the nickel, carbon being deposited. With methylamine, good results are not obtained, probably owing to the action of the hydrogen cyanide on the nickel. Copper is not such a good catalyst as nickel for this reaction. W. G.

Elements neither Free nor Combined. A Third State. CARL HERING (*J. Amer. Chem. Soc.*, 1917, **39**, 1619—1623).—A plea for the recognition of ions as representing a third state in which the elements are neither free nor combined. H. M. D.

Numerical Relationships between Atomic Weights. RUDOLF VONDRÁČEK (*Chemické listy*, 1917, **11**, 33—37; from *Chem. Zentr.*, 1917, i, 840).—The theory that certain, if not the majority, of chemical elements are mixtures of several isotopic elements of different atomic weight has not been supported by the

results of previous investigations. The approximately integral atomic weights of the elements of the series H–Co has been regarded as a consequence of genetic relationships; the author now shows that the heavy elements are related to one another as well as to those of the two short periods by definite and regular differences in the atomic weights. If the atomic weights of the elements of the two short periods the ordinal numbers of which are multiples of 3 (Li, C, F, Mg, P, Ar) are increased by 95·9, the atomic weights of the elements of the series Rh–I with uneven ordinal numbers (Rh, Ag, In, Sb, I) are derived. When the atomic weights of the same elements, with the exception of lithium and carbon, are increased by 87·7 or 88·1, the atomic weights of the elements of the series Rh–I with even ordinal numbers (Pd, Cd, Sn, Te) are obtained. A similar relationship connects the elements of uneven ordinal numbers (Ag, In, Sb, I) with those of the ordinal numbers 10, 13, 16, 19. Not only the atomic weight, but also the position of the derived element in the natural system, is accurately and definitely determined by these relationships; tellurium and iodine fall naturally into the places assigned to them on the basis of determinations of atomic weight. Similar relationships are found in other portions of the system. H. W.

Valency Centres. O. Hinsberg (*J. pr. Chem.*, 1917, [ii], **95**, 121—131).—A theoretical paper in which the author slightly modifies his earlier views (this vol., ii, 173; A., 1916, i, 725) by assuming the postulated valency centres to be identical with the positively charged atomic nuclei of the electronic theory. The atoms of the elements of groups I to IV of the periodic classification are believed to possess only one valency centre and exhibit a maximum valency of 4, although this is only occasionally exhibited before the carbon group; atoms of the elements of groups V and VI possess two valency centres or atomic nuclei, whilst atoms of group VII may possess two or three. In illustration of the theory, the nitrogen atom is cited as having two nuclei, one of which holds four valency electrons, whilst the other retains only one, and under certain conditions is capable of functioning in a similar manner to the nucleus of the univalent atom of an alkali metal, with the formation of an ammonium salt. The sulphur atom in the sulphonium compounds includes a tervalent and a univalent valency centre, to which the organic groups and the acid radicle are respectively attached. D. F. T.

The Period of the Alchemists Isaac of Holland and Jan Isaac of Holland. H. J. Holgen (*Chem. Zeit.*, 1917, **41**, 643—644. Compare this vol., ii, 198).—Evidence is adduced in support of the view that these alchemists lived in the second half of the sixteenth century. H. M. D.

Filtration with the Exclusion of Moisture and Air. G. Reddelien (*Chem. Zeit.*, 1917, **41**, 580).—A glass bell, provided with a side-tube and a tubulure at the top, is fitted over an ordinary

Büchner funnel. The side-tube is connected with absorption vessels, so that air free from moisture or carbon dioxide may be admitted into the funnel. The liquid to be filtered is introduced into the funnel through a funnel fixed in the tubulure; the stem of this second funnel is closed by a rod which is ground to fit into the stem. The join between the rim of the bell and the upper edge of the Büchner funnel is made air-tight by means of a rubber band.

W. P. S.

An Arrangement for the Automatic Washing of Precipitates Filtered with Difficulty. G. WEGELIN (*Kolloid Zeitsch.*, 1917, **20**, 270—274).—The apparatus described is a simple arrangement in which the wash liquid is supplied to the filter funnel intermittently, this being effected automatically by a syphon of the type familiar in a Soxhlet apparatus. A further feature of the apparatus is that the filtration is carried out under an excess pressure.

H. M. D.

The Use of Large Glass-stoppered Containers in Autoclaving. ROBERT B. KRAUSS (*J. Amer. Chem. Soc.*, 1917, **39**, 1512—1513).—The material which it is necessary to heat in an autoclave may be placed in a glass bottle, tightly stoppered, and this put in an iron autoclave half filled with water. Under proper conditions, the pressure on the glass is the same inside and outside, and bottles have been used in this way up to pressures of 5000 lb. per square inch.

J. C. W.

Lecture Experiments on the Theory of Explosives. J. EGGERT and H. SCHIMANK (*Zeitsch. Elektrochem.*, 1917, **23**, 189—192).—Several lecture experiments are described, which are designed to demonstrate the evolution of gas, the varied explosion velocities, and the difference between the decomposition of a primary and a secondary explosive. A further experiment is described to show the difference between deflagration and explosion.

J. F. S.

Inorganic Chemistry.

Electrolysis of Hydrochloric Acid. PAUL HANCK (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 33—34; from *Chem. Zentr.*, 1917, i, 991).—In order to avoid the absorption of chlorine during the electrolysis of hydrochloric acid, the decomposition is effected in a small U-tube provided with two side-tubes. The electrodes are held in position by rubber stoppers, and do not dip deeply into the acid. The evolved gases are conducted by rubber tubes to the Hofmann's apparatus, which is charged with concentrated sodium chloride solution. H. W.

Electrolysis of Hydrochloric Acid in Hofmann's Apparatus. FRIEDRICH C. G. MÜLLER (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 34—35; from *Chem. Zentr.*, 1917, i, 991—992).—During the electrolysis of hydrochloric acid in Hofmann's apparatus, the cathode liquid should not contain dissolved chlorine, since this is carried forward by the hydrogen; the observed volume of the latter is consequently too great.

If, during the electrolysis of sodium chloride solution, the sodium hypochlorite attains a considerable concentration around the cathode, it exerts an oxidising action and too little hydrogen is evolved. Platinum electrodes are scarcely attacked by the chlorine, whilst thin carbon rods are completely disintegrated after a short time. H. W.

When is a Candle Extinguished in an Enclosed Volume of Air? FRIEDRICH C. G. MÜLLER (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 28—30; from *Chem. Zentr.*, 1917, i, 991).—The air in which a candle has burnt until extinguished contains 4—6% carbon dioxide and 15—13% oxygen; deeply expired air has a similar composition. Alcohol, burning on cotton-wool, leaves, after extinction, a gas mixture containing 6·5% carbon dioxide and 11% oxygen. The residue from glowing wood charcoal contains 8% carbon dioxide and 9% oxygen. Burning sulphur leaves 13·5% oxygen. H. W.

The Absorption of Atmospheric Gases by Water. J. H. COSTE (*J. Soc. Chem. Ind.*, 1917, **36**, 846—853).—A summary of the work which has hitherto been done on the solubility of air in various waters, including distilled water, rain water, well water, and sea water. T. S. P.

Proof of the Formation of Water by the Union of an Acid and a Base to Yield a Salt. H. ZEITLER (*J. physikal. chem. Unterr.*, 1917, **30**, 35; from *Chem. Zentr.*, 1917, i, 991).—A small dry stick of sodium or potassium hydroxide is placed in a jar of dry hydrogen chloride. After a short time, the glass becomes strongly bedewed and the alkali is covered with crystals of salt. H. W.

The Colour and Oxidising Value of some Ozone Solutions. FRANZ FISCHER and HANS TROPSCH (*Ber.*, 1917, **50**, 765—767).—When a current of ozonised oxygen is passed through acetic acid, acetic anhydride, ethyl acetate, chloroform, or carbon tetrachloride at the ordinary temperature, a blue solution is obtained (compare Harries and Koetschau, A., 1909, i, 755; Erdmann, A., 1908, ii, 830), the colour persisting for more than fifteen to twenty hours with acetic acid and carbon tetrachloride, but disappearing more rapidly with the other solvents. Water and formic acid do not form coloured solutions, the latter solvent undergoing oxidation to carbon dioxide.

Comparative experiments with a gaseous stream containing approximately 6% of ozone by volume indicated that carbon tetra-

chloride dissolves seven times as much ozone as an equal bulk of water, and when saturated contains per litre three times as much ozone as the original ozonised oxygen.

The formation of the blue solution of ozone in carbon tetrachloride forms a simple lecture experiment. D. F. T.

Action of Ozone on Inorganic Compounds. C. HARRIES (*Zeitsch. anorg. Chem.*, 1917, **99**, 195—196).—A reply to Riesenfeld and Bencker (this vol., ii, 201). The author's experimental results are not to be explained by the high concentration of the potassium iodide solution, a 2·5% solution only having been used. The action of crude and washed ozone on butylene (A., 1912, i, 343, 407) is evidence of the presence of more than one compound in ordinary ozone. C. H. D.

Black Sulphur. BERNHARD NEUMANN (*Zeitsch. angew. Chem.*, 1917, **30**, i, 165—168).—As a result of the investigation of some black sulphur from Mexico, the author comes to the conclusion that the black sulphur of Magnus and Knapp is not a special modification of sulphur, but ordinary yellow sulphur which has been coloured black by small quantities of carbon or of metallic sulphides (iron and platinum).

The following analyses I, II, and III are of black sulphur from the San Augustin mines, IV of blackish-green sulphur from the San Rafael mines, and V of yellow sulphur from the San Rafael mines:

	S.	C.	$Fe_2O_3(Al_2O_3)$.	CaO.	MgO.	SO_3.	CO_2.	Insol.
I.	58·31	0·53	1·00	11·85	0·52	17·75	—	9·72
II.	58·63	0·59	0·78	12·16	0·82	18·90	—	7·74
III.	60·11	0·77	1·32	11·18	3·77	4·64	10·28	7·64
IV.	91·92	0·13	0·23	2·76	0·14	3·75	—	0·72
V.	99·98	—	—	—	—	—	—	0·02

The presence of carbon in the black sulphur is explicable on the assumption that the hydrocarbons in the volcanic exhalations from which the sulphur is deposited do not come into contact with sufficient air for complete combustion, with the result that carbon is deposited. The microphotographs of black sulphur show the presence of sulphur and amorphous carbon side by side. T. S. P.

Apparatus for the Preparation of Hydrogen Sulphide or Hydrogen. MOSBACHER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 176). —Hydrochloric acid is contained in a bottle situated above the other part of the apparatus, and is allowed to flow in regulated quantity into a bottle containing ferrous sulphide or granulated zinc. This bottle is provided with a delivery tube for the gas evolved, and the gas is passed through a wash-bottle before use. Spent liquor may be drawn off from the lower part of the bottle containing the ferrous sulphide or zinc. W. P. S.

Apparatus for Precipitation with Hydrogen Sulphide under Pressure. AUBREY VAIL FULLER (*J. Ind. Eng. Chem.*, 1917, **9**, 792—793).—The upper opening in an ordinary Kipp

generator is closed with a rubber stopper through which pass a small tapped tube and a narrow tube almost a metre long; a bulb is provided at the top of the latter tube. The gas outlet of the apparatus is provided with a two-way tap. The precipitation is carried out in a flask closed with a rubber stopper carrying two tubes, one of which conducts the hydrogen sulphide into the flask, whilst the other carries a length of rubber tubing and a pinch-cock. The latter is closed when the flask is filled with hydrogen sulphide, and, by closing the tap at the top of the apparatus, a pressure column of about a metre may be obtained, the liquid in the generator rising to this height in the long narrow tube. W. P. S.

The Decomposition of Metallic Sulphates by Heat. H. O. HOFMAN and W. WANJUKOW (*Bull. Amer. Inst. Min. Eng.*, 1912, 889—943; from *Zeitsch. Kryst. Min.*, 1915, **55**, 111).—The decomposition of many hydrated and dehydrated metallic sulphates has been studied by heating in an open tube in a current of dry air. The salts examined include ferric and ferrous sulphates, and sulphates of bismuth, aluminium, zinc, lead, copper, manganese, nickel, cobalt, cadmium, magnesium, silver, calcium, and barium. In each case the temperature is recorded at which decomposition begins and that at which it becomes energetic, whilst the gaseous and solid products are described. In general, normal sulphates which form no basic sulphates by decomposition give sulphur trioxide and dioxide as gaseous products, whilst those which form basic sulphates give only sulphur dioxide. By further decomposition of the basic salt into metallic oxide, sulphur trioxide is produced. Metallic sulphates of the bases of the form M_2O_3 or M_2O give no basic sulphates by decomposition. E. H. R.

The Synthesis of Ammonia and the Oxidation of Ammonia to Nitric Acid. EDWARD B. MAXTED (*J. Soc. Chem. Ind.*, 1917, **36**, 777—782).—A general account, without going into details, of the work which has been done by an English Company towards the establishment of a synthetic ammonia industry in Great Britain.

The nitrogen is separated from the air in the first case by passing the air through a separating column, over the plates of which a descending current of liquid nitrogen is allowed to flow. The oxygen is thereby liquefied and the nitrogen passes upwards, whilst the residual mixture of oxygen and nitrogen undergoes fractionation in the lower part of the apparatus; the liquid arriving at the bottom of the column is practically pure oxygen. The hydrogen (99·9% purity) is produced by a modification (not described) of the intermittent method, that is, by the alternate steaming and reduction of iron with water-gas.

The catalysts used to bring about the combination of nitrogen and hydrogen consist of iron containing traces of other substances as promoters. The working pressure is about 180 atmospheres, and the temperature in the catalyst column varies from 600° to 650°.

The oxidation of the ammonia to nitric acid is brought about by

iron catalysts containing various promoters, air, or air enriched with oxygen, being used as the oxidising agent. A table is given showing the efficiency at 700° of the following catalysts: iron, iron–thorium, iron–cerium, iron–bismuth, iron–tungsten, iron–copper, iron–lead, iron–antimony, iron–potassium, iron–uranium, iron–calcium, iron–zinc, and iron–manganese. The efficiency of pure iron is very appreciably raised by the addition of cerium, thorium, bismuth, tungsten, or copper, the time of contact for the maximum yield of nitric acid varying with the particular promoter used. The alkali metals appear to have very little effect on the activity of iron, whilst calcium, zinc, and manganese depress very considerably the maximum yield of nitric acid.

Figures are given showing that from the point of view of power and material, the direct synthesis of ammonia is twice as efficient as the cyanamide process and more than six times as efficient as the arc process. T. S. P.

The Antiseptic Properties of Nitrous Air. H. Colin (*Compt. rend.*, 1917, **165**, 194—196).—The antiseptic power attributed by Priestley (*Phil. Trans.*, 1772, **62**, 210) to nitrous air is really due to the nitric acid formed by contact with the moist air introduced with the animal corpses. W. G.

The Sensitiveness of Azides. Lothar Wöhler and F. Martin (*Zeitsch. angew. Chem.*, 1917, **30**, i, 33—39).—The azides investigated were those of silver, lead, mercury (ous), cadmium, zinc, copper (ous), nickel, cobalt, manganese, barium, strontium, calcium, lithium, and thallium. In order to determine the temperature of detonation, varying quantities (0·005, 0·01, and 0·02 gram) of the azides were heated at known temperatures in a special apparatus and the time (in seconds) noted before detonation took place. The azides were used in the form of pastilles. From the curves showing the relation between the weight of azide used and the temperature of detonation, it is found that the temperature falls with increase in weight, the curve ultimately becoming asymptotic towards the axis of weight. The temperature corresponding with the asymptotic portion of the curve is characterised by the authors as the real temperature of detonation; practically, it is the temperature found when 0·02 gram of the azide is used. The detonation temperatures of the various azides, in the order given above, were found to be 297°, 327°, 281°, 291°, 289°, 174°, 200°, 148°, 203°, 152°, 169°, 158°, 245°, and 320° respectively; the thallium azide does not detonate, but only undergoes vigorous decomposition. These temperatures do not show any well-defined regularity, but, generally speaking, the lower the molecular weight of the azide the lower is the detonation temperature. This is quite different from the behaviour of the fulminates, the detonation temperature of which (particulars to be published later) are almost independent of the metallic component. Moreover, the fulminates do not show the same tendency as the azides to give an asymptotic portion of the weight-detonation temperature curve.

The azides of zinc, cobalt, nickel, manganese, calcium, and lithium are hygroscopic.

As a result of the authors' experiments on the azides and fulminates, it is suggested that the detonation temperature for technical purposes should be defined as that temperature below which pressed pastilles of the microcrystalline substances do not detonate even after heating for five minutes; the quantity of substance should be such that it does not all decompose before the detonation temperature is reached. The comparison temperature for the different substances is defined as that at which detonation takes place when 20 mg. of the substance are heated for five seconds.

The sensitiveness of the various azides towards shock, using a falling weight, was also determined, and the curves showing the relation between the quantity of substance and the height of fall of the weight drawn. The curves often show a well defined minimum, so that for the characterisation of the azides the complete curve must be determined. The detonation temperature therefore forms a better criterion for the azides than their sensitiveness towards shock. In the case of thin layers of the azides, the sensitiveness towards shock corresponds with the Dupré friction sensitivity.

The heat of detonation has no noticeable influence on the sensitiveness of the azides. With the fulminates the parallelism between the temperature of detonation and the sensitiveness towards shock is much more marked than with the azides, which only show it between certain limits of weight of substance. T. S. P.

The Structure of Pyrophosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **99**, 190—194. Compare A., 1915, ii, 446).—Further evidence is given in favour of an unsymmetrical structure for pyrophosphoric acid. When orthophosphoric acid is dehydrated by boiling with $SOCl_2$, the pyro-acid formed is always accompanied by metaphosphoric acid, whilst when SO_2Cl_2 is used, only the pyro-acid is obtained.

Ethyl metaphosphate, prepared from ethyl ether and phosphoric oxide without heating, combines with ethyl orthophosphate at 185—190°, forming the pyrophosphate. Ethyl metaphosphate does not combine with methyl orthophosphate, but methyl metaphosphate is formed by heating methyl pyrophosphate.

Calcium pyrophosphate reacts with phosphorus pentachloride according to the equation $2Ca_2P_2O_7 + 6PCl_5 = Ca(PO_3)_2 + 8POCl_3 + 3CaCl_2$, and the strontium salt behaves in a similar manner.

C. H. D.

Production of Per-salts (Perphosphates and Perarsenates). S. ASCHKENASI (D.R.-P., 296796, 1914; from *J. Soc. Chem. Ind.*, 1917, **36**, 872).—Alkaline earth peroxides can be dissolved in excess of concentrated phosphoric or arsenic acid, forming hydrogen peroxide and the corresponding primary per-salt. The hydrogen peroxide does not decompose, and by evaporation under diminished pressure, with minimum elevation of temperature, the primary

perphosphate or perarsenate can be obtained. The corresponding alkali salts can be obtained by decomposing the alkaline earth salts before evaporation with an alkali sulphate. T. S. P.

Production of Anhydrous Per-salts or Mixtures of Per-salts. S. ASCHKENASI (D.R.-P. 296888, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 872).—Per-salts prepared in a vacuum can be subsequently dried in air at 100° without evolution of oxygen. They soften and again dry, giving off an appreciable quantity of water vapour. Drying in this way improves the stability of the per-salts. T. S. P.

Differentiation of the Internal Structure of Different Species of Silica by their Röntgen Ray Interference Patterns. S. KYROPOULOS (*Zeitsch. anorg. Chem.*, 1917, **99**, 197—200).—The method of Debye and Scherrer (*Nachr. K. Ges. Wiss. Göttingen Math.-phys. Klasse*, 1916) has been applied to powdered silica. An amorphous substance in this condition behaves as a grating of low dispersive power, whilst a powdered, crystalline substance behaves as a grating of high dispersive power. The particles used are from 0·5 to 1 μ in diameter, and are lightly pressed into paper tubes and exposed to platinum radiation. Quartz and cristobalite give similar but readily distinguishable systems of rings, whilst interference rings are absent from the patterns of quartz glass and precipitated silica. A silica gel gives a single broad ring. When precipitated silica is heated at 1300° for two hours, interference rings appear, indicating a partial conversion into cristobalite. C. H. D.

The Exchange of Bases in Silicates. I. The Exchange of Alkalis and Ammonia in Hydrated Alumina Alkali Silicates (Permutites). E. RAMANN and A. SPENGEL (*Zeitsch. anorg. Chem.*, 1916, **95**, 115—128).—Sodium permutite is purified by treating with a 10% solution of sodium chloride until calcium is no longer extracted. When small quantities of calcium carbonate are present, more rapid purification is effected by treatment with 10% ammonium nitrate, followed by reconversion of the ammonium permutite into the sodium compound. The granular permutite is freed from small particles, and the reacting solution is run through it at the rate of 50 c.c. per hour. Complete equilibrium is attained in this way.

Sodium permutite yields the same potassium permutite with potassium chloride and potassium sulphate, and the ammonium compound is also completely converted into the potassium compound. The total concentration of the solutions is without influence on the composition of the final product, which is also independent of the nature of the alkali in the original permutite. When mixed solutions of different salts are used, the resulting composition is such as to indicate that the reaction is entirely ionic. It is independent of the nature of the anion. C. H. D.

The Binary Systems of Bromides of the Alkalis and Alkaline Earths. GEORG KELLNER (*Zeitsch. anorg. Chem.*, 1917, **99**, 137—183).—The bromides are melted in Jena glass tubes in an atmosphere of nitrogen, the platinum platinum–rhodium couple being inserted without a protecting sheath. Transparent sections of the solidified mass are made by soaking in Canada balsam and grinding with paraffin. The following melting points of the anhydrous simple bromides are found: LiBr, 552°; NaBr, 742°; KBr, 730°; $MgBr_2$, 711°; $CaBr_2$, 730°; $SrBr_2$, 643°; $BaBr_2$, 847°. All are isomorphous with the corresponding chlorides, with the exception of strontium bromide, which is hexagonal, the chloride being regular. Dimorphism has not been observed. Lithium bromide forms with sodium bromide a continuous series of solid solutions, which probably break up at lower temperatures, as, although thermal or crystallographic changes have not been observed, the crystalline mass expands and disintegrates on cooling. Lithium and potassium bromide form a simple system without solid solutions, the eutectic temperature being 348°. Lithium bromide forms solid solutions of limited concentration with both magnesium and calcium bromides, the liquidus curves being of similar and rather unusual form. With strontium bromide, a double salt, $LiBr,2SrBr_2$, is formed, decomposing at 503°. Lithium and barium bromides have a eutectic point at 483°, and solid solutions are not formed.

Sodium and magnesium bromides form a simple eutectiferous series, the eutectic temperature being 431°. Sodium and calcium bromides solidify to form two series of solid solutions, with a eutectic point at 513°, and, on further cooling, a reaction takes place at 469°, a compound, $NaBr,2CaBr_2$, being formed. Sodium bromide forms simple eutectiferous systems with both strontium and barium bromides, the eutectic temperatures being 486° and 600° respectively.

Potassium bromide forms double salts with all the bromides of the alkaline earths. The compounds $2KBr,MgBr_2$ and $KBr,MgBr_2$ decompose at 348° and 391° respectively, and there is a eutectic point between them at 334°. Solid solutions are not formed in this or the following series. Only a single compound is formed with calcium bromide, $KBr,CaBr_2$, represented by a maximum on the freezing-point curve at 637°. There are eutectic points at 544° and 563° respectively. In the strontium series there are two flat maxima, $2KBr,SrBr_2$, freezing at 559°, and $KBr,2SrBr_2$, at 574°. There are thus three eutectic points, at 556°, 534°, and 562° respectively. One flat maximum at 634° occurs in the barium series, corresponding with the compound $2KBr,BaBr_2$, and the eutectic temperatures are 632° and 612°.

C. H. D.

The Dissolution of Sodium Chloride Crystals in Solutions containing Carbamide. WALTER SCHNORR (*Zeitsch. Kryst. Min.*, 1915, **54**, 289—331).—The author has carried out an

exhaustive series of experiments on the manner in which a crystal of common salt dissolves when placed in an unsaturated salt solution, with particular reference to the effect of the presence of varying quantities of carbamide, which is known to influence the habit of growth of such crystals. It is found that, if growth and dissolution take place in presence of the same quantity of carbamide, sharp corners develop during solution at the poles of those faces which predominate in the growing crystal. The velocity of solution of each face is dependent on the degree of unsaturation of the solution and on the quantity of carbamide present. The differences in solution–velocity between different faces diminish as the degree of unsaturation increases, but are enhanced by increase in the quantity of carbamide, particularly with respect to the vicinal icositetrahedron and octahedron faces. The form of the final body also depends, in many cases, on the form of the crystal first placed in the unsaturated solution. E. H. R.

Polymorphism of Ammonium Nitrate. FRÉD. WALLERANT (*Bull. Soc. franç. Minéral.*, 1916, **39**, 162—163; from *Chem. Zentr.*, 1917, ii, 6).—The author maintains the correctness of his previous observations (A., 1906, ii, 152). The discrepancies between his results and those of Behn (*Proc. Roy. Soc.*, 1908, [A], **80**, 444) between 82° and −16° are probably attributable to differences in the methods of investigation, as, for example, occurrence of under-cooling. H. W.

Ammoniates of Silver Salts. III. G. BRUNI and G. LEVI (*Gazzetta*, 1917, **47**, i, 259—272. Compare A., 1916, ii, 482, 617). —The following thermochemical data have been arrived at experimentally. Molecular heats of solution in water: $AgNO_3$, −5·30 Cal. (1 gram-mol. in 1000 mols. H_2O) or −5·70 Cal. (1 gram-mol. in 1600 mols. of water); $AgNO_3,2NH_3$, −9·05 Cal.; $AgNO_3,3NH_3$, −10·44 Cal.; $AgClO_4$, −2·17 Cal.; $AgClO_4,2NH_3$, −10·71 Cal.; $AgClO_4,3NH_3$, −11·18 Cal. Heats of formation in solution: $AgNO_3+2NH_3+aq.=+12·68$ Cal.; $AgClO_4+2NH_3+aq.=+12·71$ Cal. Heats of formation in the solid state: $AgNO_3+2NH_3=$ +33·64 Cal.; $AgNO_3+3NH_3=42·94$ Cal.; $AgClO_4+2NH_3=+38·40$ Cal.; $AgClO_4+3NH_3=+47·77$ Cal. (compare Berthelot and Delépine, A., 1899, ii, 748).

These results indicate that only the diammoniates exist in solution. The triammoniates, which exhibit considerable heats of formation in the solid state, are completely decomposed in solution into the corresponding diammoniates and free ammonia.

Measurements of electromotive force indicate the existence in solution of the complex $Ag(NH_3)_2$, and of this alone, even in ammoniacal solutions of silver nitrite. The compound, $AgNO_2,NH_3$, is consequently regarded as the double salt, $AgNO_2,(AgNO_2,2NH_3)$, and a similar explanation may hold for the compound $AgNO_3,NH_3$. T. H. P.

Saturated Solutions of Potassium and Magnesium Sulphates. H. S. VAN KLOOSTER (*J. Physical Chem.*, 1917, **23**, 513—518).—Van't Hoff has indicated that polyhalite,

$$Ca_2MgK_2(SO_4)_4,2H_2O,$$

can co-exist in equilibrium at 25° with any two of the following substances: syngenite, $CaK_2(SO_4)_2,H_2O$; reichardtite,

$$MgSO_4,7H_2O;$$

and gypsum, $CaSO_4,2H_2O$. He suggests that at some temperature below 25° polyhalite will break up into the three above-mentioned salts. The present author has undertaken to investigate this point, and, having found not inconsiderable discrepancies in the work of Basch (*Diss.*, *Berlin*, 1901), he has as a preliminary re-determined the solubility curve of potassium magnesium sulphate at 25°. The experimental details are given in the paper, and it is especially pointed out that the conclusions of van't Hoff, which are based on the determinations of Basch, are of questionable accuracy. J. F. S.

Phosphorescent Zinc Sulphide. (MISS) ELIZABETH MACDOUGALL, ALFRED WALTER STEWART, and ROBERT WRIGHT (T., 1917, **111**, 663—683).—An investigation in which the nature and cause of the phosphorescence of zinc sulphide are examined. It is shown that pure zinc sulphide, prepared in various ways, can be obtained in a phosphorescent condition. The addition of certain impurities has a marked effect, in some cases, as with iron, inhibiting the action, and in others, for example, manganese, altering the tint of the phosphorescence. The presence of a chloride always improves the phosphorescence. The temperature to which the preparation has been heated has the greatest influence on the phosphorescence. This temperature may be varied within limits, but in general the best results are obtained at temperatures between 650° and 900°. Washing, rubbing, or disturbing the final product in any way tends to diminish its phosphorescent power. Amorphous zinc sulphide is non-phosphorescent, and the crystalline variety does not give such marked effects as the semi-crystalline samples. The phosphorescence of specimens of zinc sulphide made from salts containing no chloride is not so brilliant as that of specimens produced in the presence of chlorides. The experiments show that phosphorescence is much influenced by physical conditions, and cannot be regarded as entirely due to the chemical nature of the phosphorophore. Thus it is established that the strongest phosphorescence is observed in specimens which are just on the border between the amorphous and crystalline conditions, and this state can be attained either by heating for a very short period at a high temperature or for a longer period at a lower temperature. The fact that washing diminishes the phosphorescence indicates the probable presence of some material which has a strong influence on the phenomenon. Since crushing, grinding, or rubbing of the final product also decreases the phosphorescence, it seems probable that the supposed impurity forms a skin over

the particles of the sulphide, which is removed by washing or disintegrated by mechanical treatment. It appears from the evidence that the chloride ion may be the cause of the enhanced phosphorescence due to impurity. This may act in the following way: When the impure sulphide is heated, the chloride reacts with it and produces a surface film of zinc chloride on the sulphide, and this film, on cooling, may contract and produce a strained condition of the material within the film. The effect of additional impurities would be to influence the fusibility of the sulphide and chloride, and it may be in this action that the main influence of the impurities is to be sought. J. F. S.

The Solubility of the Salts of Isotopic Elements. K. FAJANS and J. FISCHLER (*Zeitsch. anorg. Chem.*, 1916, **95**, 284—296).—On the assumption that saturated solutions of corresponding salts of isotopic elements must contain the same number of molecules in equal volumes, it follows from the different molecular weights that the solubilities expressed in grams per litre and the densities should be different. This has been tested by means of lead nitrate prepared from ordinary lead of atomic weight 207·15 and lead from carnotite with atomic weight 206·59 (Richards and Lembert, A., 1914, ii, 653), the nitrates being purified by repeated recrystallisation in platinum vessels. The determinations of solubility are made in Jena-glass vessels in a thermostat constant to 0·02°, equilibrium being reached from both sides, for which two days are necessary. Direct analytical determinations of the lead in the two solutions give results which differ by less than the possible error, but the more exact method of determining the density of the solutions shows that there is a real difference, ordinary lead nitrate being the more soluble, but the values differ by less than 0·1% (compare A., 1915, ii, 207).
C. H. D.

A Method for the Relative Atomic Weight Determinations of Isotopic Elements. K. FAJANS and M. LEMBERT (*Zeitsch. anorg. Chem.*, 1916, **95**, 297—339. Compare preceding abstract). —If saturated solutions of the nitrates of two lead isotopes contain the same number of molecules per litre, which is the case if the ratio of molecules of salt to molecules of water is the same, the molecular volumes being identical and the change of volume on solution also the same, the relative atomic weights may be determined from measurements of the solubility. The difference in weight between equal volumes of the two solutions is in the same ratio to the mean lead content as the difference of atomic weight to the mean atomic weight.

An electrically heated thermostat is used, the mercury contact of the regulator being provided with a small automatic hydrogen generator to prevent fouling of the mercury. The temperature is maintained at 24·45°±0·002°. One end of the improved pyknometer is closed with a tap and the other with a narrow, ground-

on tube. In all cases at least three days are allowed for the attainment of equilibrium. The nitrates used are prepared from ordinary lead (atomic weight 207·15), carnotite lead (206·59), and lead from Joachimsthal pitchblende (206·57), all being repeatedly recrystallised, the removal of nitric acid being specially important. The following values are found for $D_4^{24\cdot45}$: ordinary lead nitrate, $1\cdot444499 \pm 0\cdot000013$; carnotite lead, $1\cdot443587 \pm 0\cdot000016$; pitchblende lead, $1\cdot443586 \pm 0\cdot000015$. The molar solubilities are, within the experimental error, identical. The values for the difference in weight of 10 c.c. of the two saturated solutions are: for ordinary and carnotite lead, $9\cdot04 \pm 0\cdot26$ mg., and for ordinary and pitchblende lead, $9\cdot35 \pm 0\cdot52$ mg., the values found experimentally being respectively $9\cdot12 \pm 0\cdot29$ and $9\cdot13 \pm 0\cdot28$ mg. The agreement is sufficiently close to justify the use of the method for determining relative atomic weights.

The definition of an element is discussed in relation to these and similar observations. C. H. D.

Sodium-Lead Compounds in Liquid Ammonia Solution. F. HASTINGS SMYTH (*J. Amer. Chem. Soc.*, 1917, **39**, 1299—1312).—The nature of the compounds which are formed when metallic lead is dissolved in liquid ammonia containing sodium has been investigated by electrolysing the solutions with a platinum gauze anode and a lead cathode. Measurements of the gain in weight of the anode and the loss in weight of the cathode were made in a series of experiments with solutions which had been previously saturated with lead. The results show that 2·26 gram-atoms of lead are deposited at the anode and dissolved at the cathode for each faraday passed through the solution. This value is independent of the concentration of the solution between the limits of 0·01 and 0·1 mol. of sodium per litre, and is also independent of the magnitude of the current.

Measurements of the solubility at $-33°$ of lead in liquid ammonia containing varying amounts of sodium show also that more than two atoms of lead are dissolved for each atom of sodium present.

The electrolytic and solubility data lead to the conclusion that the solutions examined contain an equilibrium mixture of electrolytes of the formulæ $NaPb_2$ and $NaPb_3$. If these are equally ionised, the value of the ratio $[Pb_3']/[Pb_2']$ is about 0·36.

The compound containing the larger proportion of lead is more soluble in liquid ammonia than the other, and has not been isolated. When the solutions are evaporated, the vapour pressure falls until solids begin to separate, when the pressure remains constant until the solvent has completely disappeared, when it falls to zero. The deposited solid is not therefore an ammonia compound. H. M. D.

The Crystal Structure of the Compound $H_{10}Tl_2B_{12}O_{24}$. RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1914, **54**, 232—237).—A fresh examination of the crystals of this thallium borate, pre-

pared by Buchtala (A., 1914, ii, 135), shows it to be monoclinic [$a:b:c=1{\cdot}5827:1:1{\cdot}9546$; $\beta=94^\circ25'$). The crystals form curious twins, which have been examined goniometrically and optically.

Buchtala gives to this compound the formula $Tl_2B_{12}O_{19},5H_2O$, but the author considers that the water is probably water of constitution, not water of crystallisation. The formula then becomes $2(H_5TlB_6O_{12})$, and may be written

$$OH{\cdot}B{<}^{O\cdot B(OH)\cdot O\cdot B(OH)\cdot O}_{O\cdot B(OH)\cdot O\cdot B(OH)\cdot O}{>}B{\cdot}OTl.$$

The further series of thallium borates prepared by Buchtala, $Tl_2B_2O_4,H_2O$, $Tl_2B_4O_7,2H_2O$, $Tl_2B_6O_{10},3H_2O$, $Tl_2B_8O_{13},4H_2O$, may be regarded as an homologous series of the general formula $Tl_2O[HBO_2]_{2n}$, in which the boron atoms, linked together by oxygen atoms, form a chain, for example,

$$Tl{\cdot}O{\cdot}B(OH){\cdot}O{\cdot}B(OH){\cdot}O{\cdot}Tl.$$

E. H. R.

The System Iron–Copper. RUDOLF RUER and FRANZ GOERENS (*Ferrum*, 1916, **14**, 49—61; from *Chem. Zentr.*, 1917, i, 1065. Compare Ruer and Fick, A., 1914, ii, 274).—With the object of elucidating certain discrepancies, particularly in regard to the behaviour of the molten metals, the authors have melted electrolytic copper and iron (m. p. 1528°) in porcelain tubes in an atmosphere of nitrogen, and have investigated the alloys thermally, micrographically, and magnetically. A separation of layers actually occurs when the pure metals are melted together. On the other hand, that portion of the freezing-point curve which lies between the end-points of the mixture gap (24% Cu at 1450° and about 85% Cu at 1375°) is definitely shown not to be horizontal; the observed discrepancy cannot be attributed to under-cooling. On solidification, therefore, the system Fe–Cu shows the behaviour of a system of three or more substances. The absorption of impurities during the process of melting, in amount sufficient to explain the phenomena, could not be established. It must therefore be assumed that a molecular complex is formed which, on account of its slow velocity of production and decomposition, plays the part of a third substance, but further confirmation of this view was not obtained. Apparently an inexplicable contradiction of the phase rule is here presented. For further details, the tables and diagrams of the original communication must be consulted.

H. W.

A Colourless Modification of Mercuric Iodide. G. TAMMANN (*Nach. K. Ges. Wiss. Göttingen*, 1916, 292—293; from *Chem. Zentr.*, 1917, i, 1065).—If mercuric iodide is heated at about 300—500° in a long glass tube, one end of which is connected to a receiver in which the pressure can suddenly be decreased from 1 to 1/10th atmosphere, it condenses in the form of a colourless snow, which becomes pink in a few seconds and red after some minutes. The existence of such a colourless modifica-

tion corresponds with the analogy between mercury and cadmium and zinc in the periodic system. H. W.

Decomposition of Cerous Oxalate in a Reducing or Inert Atmosphere and a New Property of the Higher Oxides of Cerium. WALLACE S. CHASE (*J. Amer. Chem. Soc.*, 1917, **39**, 1576—1582).—By heating cerous oxalate at 550° in an atmosphere of hydrogen or nitrogen, a bluish-black, amorphous substance is obtained which consists of a mixture of the oxides CeO_2 and Ce_4O_7 and free carbon. When the decomposition has been carried out in an atmosphere of hydrogen, the residue takes fire when brought in contact with the air. The phenomenon is attributable to the oxidation of hydrogen, which is adsorbed in large quantities by the mixture resulting from the thermal decomposition of the cerous oxalate. Other gases are also adsorbed in marked degree by the oxides of cerium which are produced in this reaction. H. M. D.

The Changes in Physical Properties of Aluminium with Mechanical Work. II. Specific Heats of Hard and Soft Aluminium. F. J. BRISLEE (*Trans. Faraday Soc.*, 1916, **12**, 57—62. Compare A., 1913, ii, 963).—Aluminium containing 0·4% of impurities has been examined in the form of square bars, drawn rod, and wire drawn until any further attempt at extension results in fracture. The specific heat is then determined for each specimen by means of a water calorimeter. The following values are found for the annealed metal: between 20° and 300°, $0{\cdot}2354 \pm 0{\cdot}00033$; between 20° and 200°, $0{\cdot}2240 \pm 0{\cdot}0004$. The hard, brittle wire gives the value 0·2220 for the range 20—100°, but this becomes less after heating for days or weeks at 100°, the tensile strength diminishing at the same time and the brittleness disappearing. C. H. D.

Constitutional Relation of Ultramarines with other Silicates. LAURENZ BOCK (*Zeitsch. angew. Chem.*, 1917, **30**, i, 161—164).—The author gives the results of a long series of experiments, which have extended over several years, in which various silicates have either been boiled with an aqueous solution of sodium or potassium sulphide or polysulphide, or else the dry substances have been heated together. The silicates investigated included precipitated silicic acid, sodium silicate (water-glass), kaolin, various zeolites, silicates of the nephelin group, etc.

Some of the conclusions arrived at are that the ultramarines should be considered as aluminium silicates analogous to the zeolites, in common with which they possess the property that the alkali bases can be replaced by other bases. Ultramarines are formed from the zeolites by replacing water by sulphide, from which it follows that the water in the zeolites is chemically combined. Silicates of different constitution, but with similar alumina–silica ratios, the so-called alumina double silicates, for

example, sodalite, and analcime, give a partial formation of ultramarine, owing to the action of the alkali giving rise to some alumino-silicate (Aluminatsilicat). Silicates of the nephelin group also give rise to the partial formation of ultramarine, but generally only after deep-lying changes in the constitution have taken place. Ultramarines in which sodium is replaced by other bases cannot be prepared directly, but only by substitution methods. Ultramarine-violet and ultramarine-red are not definite chemical individuals; the violet is a transition stage to the red, which, as far as the constitution of the silicate is concerned, is totally different from the original ultramarine-blue.

The natural formation of hauyn and lapis lazuli has probably taken place in a similar way to that in which the weakly coloured ultramarines are obtained in the laboratory from minerals allied to the zeolites. T. S. P.

Alloys of Manganese with Gold. L. Hahn and S. Kyropoulos (*Zeitsch. anorg. Chem.*, 1916, **95**, 105—114).—Gold and manganese, the latter containing 5% of aluminium as well as other impurities, are heated together in nitrogen, the fusion being kept for as short a time as possible at 1300° before determining the cooling curve, as otherwise the sheath of the thermocouple is rapidly corroded. In all cases a temperature interval has been observed during freezing. Even in the case of the pure metals this amounted to 5° for gold and 17° for manganese. The freezing-point curve of the series has a maximum at 50 atomic %, with minima at 33 and 75 atomic % of gold respectively. The crystals exhibit cores, but form only a single solid solution. They do not become homogeneous on alloying for five hours at 700°, or one hour at 1000°. The hardness falls with the addition of gold, reaching a minimum at the first minimum freezing point. It then increases slightly up to the maximum on the freezing-point curve and then falls regularly. The thermal and hardness results are not in accordance with those obtained by Parravano (A., 1915, ii, 690).

Boiling the alloys with water leads to the formation of manganese dioxide. The same result occurs with 20% hydrochloric acid, so that chlorine is liberated and gold passes into solution, but is reprecipitated as long as manganese remains. The curves for the ratio of dissolved and undissolved manganese approach more nearly to the form required by Tammann's theory (A., 1915, ii, 427) as the time of action is increased. C. H. D.

The Carburation of Iron by Alkali Cyanides and Cyanates. A. Portevin (*Compt. rend.*, 1917, **165**, 180—182. Compare A., 1915, i, 944).—Working with mixtures of potassium cyanide and cyanate in varying proportions, and at temperatures from 750—900°, the time of heating being two or four hours, the author finds that the maximum carburation of iron is not attained when potassium cyanide alone is used, but when the mixture contains from 25—40% of potassium cyanate. W. G.

The Tempering of Steel. Henry Le Chatelier (*Compt. rend.*, 1917, **165**, 172—174).—The author considers that the work of Portevin (compare this vol., ii, 372), Chevenard (compare this vol., ii, 414), and Dejean (compare following abstract) affords experimental proof of the theory of tempering put forward by André Le Chatelier (compare *Bull. Soc. Encouragement*, 1895, 1340). W. G.

The Formation of Troostite and Martensite. P. Dejean (*Compt. rend.*, 1917, **165**, 182—185).—With a rapid tool steel containing 18% of tungsten and 4% of chromium, varying the initial temperature of cooling, but not the velocity of cooling, the cooling curves show a thermal critical point, *A*, at from 800° to 700° when the initial temperature of cooling varies from 850° to 900°. When the initial temperature of cooling passes 900°, a second point, *B*, appears at a little above 400°, and at an initial temperature of 980° the point *A* has completely disappeared. Similar phenomena have been obtained with a large number of steels, particularly the "self-tempering" steels, by suitably modifying the temperatures of heating and the velocities of cooling. Those steels which show the point *A* are found to contain perlite or troostite, those which show the point *B* martensite, and those which show both *A* and *B* are composed of troostite and martensite. Working with carbon steels and varying the velocities of cooling, the author finds that between 700° and 500° they show a point analogous to *A*, and at lower temperatures ($<$ 200°) a point which is probably related to *B*.

There is no discontinuity between the point of formation of perlite and that of troostite, these two constituents being formed of an aggregate of ferrite and cementite, the perlite containing almost all the carbon of the steel, the troostite only a portion. Below the point *A*, the carbon remaining in solution in the iron round the troostite maintains it in the form of austenite, until at the point *B* this is transformed into martensite. In order completely to suppress the formation of troostite and obtain pure martensite, with a given velocity of cooling it is necessary to pass the critical point of heating by an amount which is greater in proportion as the velocity of cooling is slower. W. G.

The Classification of Nickel Steels and Manganese Steels. P. Dejean (*Compt. rend.*, 1917, **165**, 334—337).—The nickel steels containing less than 25% of nickel, which are said to be irreversible, should really be divided into two classes, namely: (1) the perlitic steels with 0—10% of nickel, which are pseudo-reversible; (2) the martensitic steels containing 10—25% of nickel, which constitute the true irreversible steels. The same holds good for low carbon, manganese steels. Steels containing 0—3·5% of manganese are perlitic and give the point *A*; those containing from 3·5—11% of manganese are martensitic and give the point *B*. There is also an intermediate zone at 3·5—4% manganese in which

the steels have the two points *A* and *B*, and are formed of troostite and martensite. As the carbon content rises to 0·7—1·0%, this intermediate zone becomes of considerable importance. With equal manganese content, the temperature of point *A* rises and that of point *B* falls, and finally, by suitable cooling, it is possible to produce the point *A* in steels for which the point *B* is below 0°. Thus steels with troostite and austenite are obtained. W. G.

Studies in Alloys Resistant to Sulphuric Acid by Improvement of the Resistance of Nickel. ROLAND IRMANN (*Metall und Erz.*, 1917, **14**, 21—30, 37—42; from *Chem. Zentr.*, 1917, i, 1069—1070. Compare A., 1916, ii, 530).—On the assumption that metallic alloys behave towards acids and other electrolytes as aggregates of small galvanic cells the poles of which are formed by the constituents of the alloy, it is possible to obtain information regarding the behaviour of the alloy by the study of cells composed of its constituents. If the cell Ni,Cu,H_2SO_4 (50° Bé.) is short-circuited at 90°, the copper is unattacked and nickel dissolved; the potential sinks rapidly from 0·55 to 0·25 volt. The same is true for other combinations of elements, one component being invariably unprotected. Stable alloys are only to be expected when new constituents appear either as mixed crystals or chemical compounds.

Nickel–Copper.—The series of alloys (uninterrupted series of mixed crystals) shows a maximal resistance to sulphuric acid (50° Bé., 95°) at 50%; nickel is almost exclusively dissolved.

Nickel–Tungsten–Copper.—The three metals cannot be alloyed in all proportions. With increasing tungsten content, the receptivity for copper diminishes. Four alloys have been prepared containing respectively 2·11% W, 48·70% Cu; 3·22% W, 36·25% Cu; 5·12% W, 42·26% Cu; 9·57% W, 39·28% Cu. Formation of layers only occurred in one instance, the compositions being 2·23% W, 66·88% Cu, and 5·80% W, 45·10% Cu. The ternary alloy is far more stable towards acid than the nickel–tungsten alloy, particularly when containing 2% W, 20% Cu; 5% W, 45% Cu, or 10% W and 15% Cu. It has a high electrical resistance; the smallest value observed was higher than that of constantan, whilst the highest was as great as that of the best resistance material (except chromium–nickel). The strength of the moulded alloys is very considerable. The alloys can be readily rolled, those which are most resistant to acid being the best in this respect. An increase in the tungsten content would probably cause increased stability towards acid and higher electrical resistance.

Nickel–Tungsten–Copper–Iron.—The alloys were prepared by adding increasing quantities of iron wire (up to 10%) to the Ni–Cu–W alloy (*circa* 44% Cu and 3·9% W). Slight separation occurred with slow cooling. The stability towards sulphuric acid (50° Bé.) increases markedly with increasing iron content (2—10 times); traces of nickel, but neither iron nor copper, pass into solution. With more concentrated acid, corrosion is more pro-

nounced. The mechanical properties are greatly improved by the addition of iron, but the electrical resistance is scarcely affected. The favourable behaviour of alloys containing iron enables ferro-tungsten to be used instead of the expensive tungsten.

Copper–Nickel–Zinc–Tungsten.—If tungsten (1—3%) is added to Cu–Ni–Zn alloy, a separation occurs; the upper layer contains Ni–Cu–Zn, rich in copper; the lower consists of Ni–W or Ni–W–Cu, rich in tungsten. Only small quantities of tungsten (up to 0·39%) could be brought into the alloy by addition of Cu–Zn to Ni–W. No improvement could be effected in the stability of the Cu–Zn–Ni alloy towards acid, all the specimens being powerfully attacked and covered with a layer of sulphate. H. W.

Action of Metaphosphoric Acid on the Oxides of Molybdenum. A. COLANI (*Compt. rend.*, 1917, **165**, 185—187).—When molybdenum trioxide is heated with metaphosphoric acid to a dull red heat, it undergoes a very slight reduction, the loss in oxygen corresponding with the formation of the hypothetical oxide Mo_6O_{17}. When molybdenum dioxide is similarly heated, it yields the lower oxide Mo_2O_3, which gives the metaphosphate, $Mo_2O_3,3P_2O_5$, and a higher oxide, which under the experimental conditions remains dissolved in the metaphosphoric acid. W. G.

New Sulphides of Molybdenum. F. MAWROV and M. NIKOLOV (*Zeitsch. anorg. Chem.*, 1916, **95**, 188—193).—*Molybdenum pentasulphide*, Mo_2S_5, is obtained in a hydrated form by reducing a solution of ammonium molybdate, containing more than 20% of sulphuric acid, with zinc, until the colour is dark red, and then diluting, filtering, and saturating with hydrogen sulphide. The precipitate is collected and washed with hot water and then with alcohol. It is then shaken repeatedly with carbon disulphide, washed with ether, and dried at 68—75°. Analysis gives the composition $Mo_2S_5,3H_2O$. One molecule of water is lost at 135—140°, but further heating causes decomposition.

The hydrated sulphide dissolves in warm solutions of alkali sulphides to bright red solutions, depositing an orange precipitate on cooling. It dissolves with difficulty, but completely, in warm, concentrated hydrochloric acid.

Careful heating in carbon dioxide gives the anhydrous sulphide, Mo_2S_5, which is almost black. When the hydrated compound is heated in hydrogen sulphide, an exchange of water for hydrogen sulphide takes place, and the compound $2Mo_2S_5,3H_2S$ is formed. C. H. D.

Atomic Weight of Zirconium. FRANCIS P. VENABLE and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1917, **39**, 1598—1608).—The value of 90·6 adopted by the International Committee for the atomic weight of zirconium is obtained by a more or less arbitrary combination of the results obtained in nine previous determinations. These results show considerable divergence, and in the

authors' opinion little dependence is to be placed on any of the values, since it is very probable that the methods employed involve errors other than those which may be described as accidental. The oxide is involved in most of these determinations, and the loss of this on ignition represents an inherent source of error the effect of which is to give a value for the atomic weight of zirconium which is less than the true value. In the experiments described, the atomic weight is based on the determination of the ratio $4Ag:ZrCl_4$.

Zirconium hydroxide was dissolved in concentrated hydrochloric acid and the oxychloride separated by crystallisation. This was then recrystallised from hydrochloric acid some forty times, and then several times from water in quartz vessels. The oxide obtained from the oxychloride was then heated at 450—500° in a current of chlorine which had been passed through carefully purified and dried carbon tetrachloride, and by a process of fractional sublimation the last traces of iron were removed. The nephelometric determination of the ratio $4Ag:ZrCl_4$ gave a mean value of 91·76 for the atomic weight of zirconium, which is more than one unit higher than the present accepted value. The authors consider that the error in their determination is not greater than 0·1.

Attempts to determine the atomic weight from the ratio $ZrCl_4:ZrO_2$ gave a mean of 92·1, but this is admittedly too high on account of the retention of chlorine by the oxide.

The density of zirconium chloride was found to be 2·803 and of the oxide 5·49. H. M. D.

Fusion of Zirconium Dioxide and the Preparation from it of Apparatus. Emil Podszus (*Zeitsch. angew. Chem.*, 1917, **30**, i, 17—19).—Zirconium dioxide, on account of its resistance towards acids and alkalis, its small conductivity for heat, its small coefficient of expansion, and its resistance to the action of heat, should be a very suitable substance for making chemical apparatus, but hitherto the results have not been satisfactory, cracks readily developing in the finished articles. The author has now found that if the zirconium dioxide is first melted in a special arc furnace and the solidified fusion then finely ground, the powder so obtained can be used for making apparatus similar to porcelain ware, which apparatus is perfectly sound and does not develop cracks. Preliminary fusion seems to be a necessary condition for obtaining sound apparatus, although the solidified fusion is crystalline and not amorphous. The fused mass is not transparent, and is broken up and powdered only with great difficulty.

Fused zirconium dioxide has D 5·89 and a hardness between that of quartz and corundum. Three determinations of the m. p. gave 2950°, 2950°, and 3000°, the last temperature being obtained with a very pure product; impurity to the extent of $\frac{1}{5}$% will lower the m. p. by 100°. When pure, it is practically white in colour, but generally it is coloured yellow, since it readily takes up traces of

iron; also, if slight reduction of the pure oxide takes place, a yellow colour is produced.

A special furnace is described, made of the fused oxide, in which it was possible to obtain temperatures of 2400—2500°, using coal gas and oxygen for heating. The possibility of obtaining temperatures up to 3000° in the middle of such a furnace is indicated.

T. S. P.

Tantalum Chloride with Reference to its Use in the Determination of the Atomic Weight of Tantalum. GEORGE W. SEARS (*J. Amer. Chem. Soc.*, 1917, **39**, 1582—1587).—Experiments made with carefully purified tantalum chloride show that it is quite stable in an atmosphere of dry nitrogen or air, that it does not occlude chlorine, but that it undergoes hydrolysis in an atmosphere which has not been thoroughly dried by means of phosphoric oxide. On account of the readiness with which hydrolysis occurs, the author considers that tantalum chloride is not suitable for use in atomic weight determinations. H. M. D.

The Properties of Solid Solutions of Metals and of Intermetallic Compounds. F. C. THOMPSON (*Trans. Faraday Soc.*, 1916, **12**, 23—29. Compare A., 1916, ii, 601; Desch, A., 1915, ii, 561).—Considering the similarity of the properties of a metal in the cold-worked condition and in solid solution, crystalline distortion may be assumed to be present in both cases. In a solid solution, the distortion is due to an attempted equalisation of the atomic volumes of the metals crystallising together. The stress may be calculated from the two atomic volumes and the coefficients of cubical expansion of the components. A calculation for an alloy containing atomic proportions of gold and silver shows that the values obtained are of the right order. The theory leads to a parabolic curve for the hardness of a series of solid solutions, with a maximum at equal atomic proportions. The hardness and fragility of intermetallic compounds are similarly explained. C. H. D.

Preparation of Colloidal Gold Solutions by the Nucleus Method. JOSEF REITSTÖTTER (*Koll.-Chem. Beiheftr.*, 1917, **9**, 221—258).—According to Zsigmondy (A., 1906, ii, 679), it is possible to bring about an increase in the size of colloidal particles of gold by adding a small quantity of a colloidal solution to a solution of a gold salt in presence of a suitable reducing agent. Under favourable conditions, no new particles are formed, but the reduced gold is deposited on the particles already present.

This method has been further investigated, and it has been found that deep red colloidal solutions may be obtained by inoculation of an acid or slightly alkaline solution of gold chloride and reduction by means of hydrazine or hydroxylamine. The number of colloidal particles in the resulting solution is proportional to the number of nuclei in the sol used for inoculation.

By this method of increasing the size of the colloidal particles, it is possible to ascertain the number of amicroscopic particles in a given colloidal solution.

Previous observations have shown that colloidal gold particles of the smallest size are obtained by the use of an ethereal solution of phosphorus as reducing agent. Systematic attempts to ascertain the conditions favourable to the formation of the most finely divided sol have shown that particles less than 2—3·5 $\mu\mu$ cannot be obtained by this method. Incidentally, the influence of foreign substances on the spontaneous formation of colloidal gold and on the rate of increase in size of the particles has been examined.

H. M. D.

Platinum and Illuminating Gas. F. MYLIUS and C. HÜTTNER (*Zeitsch. anorg. Chem.*, 1916, **95**, 257—283).—When a luminous coal-gas flame comes in contact with platinum, a black layer is formed, and after the carbon has been burnt off in air the metal is left in a rough and brittle state, without loss of weight. The influence of different metallic impurities is examined by heating pieces of foil in Jena-glass tubes in a stream of coal gas under comparable conditions. The action is greatly increased by the presence of iron or rhodium in the platinum, iridium having less effect. Of the pure metals, rhodium has the greatest effect, followed by palladium, iridium being much less active.

When a thin jet of luminous gas flame plays on a platinum surface, concentric black rings are formed, the position of which corresponds with the different zones of the flame. Synthetic coal gas, composed of methane, ethylene, carbon monoxide, and hydrogen, is without action on pure platinum or platinum–iridium, but blackens commercial platinum. The introduction of a small quantity of carbon disulphide or sulphur dioxide causes blackening. Iridium powder, heated gently in a stream of coal gas saturated with carbon disulphide, causes the formation of a black mass containing carbon and sulphur many times the weight of the iridium. Rhodium takes up sulphur from carbon disulphide even at 100°, and the corrosive action of coal gas on commercial platinum is distinctly traced to the presence of carbon disulphide in the gas. When a sufficient quantity of oxygen is present, as in the Bunsen flame, the action of sulphur and carbon is suppressed, and the corrosion which takes place is due to oxygen, and is very small for pure platinum, but is increased by the presence of iron or iridium (compare Burgess and Waltenberg, A., 1916, ii, 442).

C. H. D.

Rhodium. A. GUTBIER and A. HÜTTLINGER (*Zeitsch. anorg. Chem.*, 1916, **95**, 247—252).—Rhodium begins to react with chlorine at 250°, forming the trichloride, $RhCl_3$. Bromine begins to react at the same temperature, but the product varies in composition, suggesting that the tribromide, $RhBr_3$, is formed and again dissociates.

C. H. D.

The Action of Oxygen on Rhodium. A. GUTBIER, A. HÜTTLINGER and O. MAISCH (*Zeitsch. anorg. Chem.*, 1916, **95**, 225—246).—When rhodium is heated in air or oxygen at temperatures from 600° to 1000°, the product is always the oxide, Rh_2O_3, the rate of oxidation increasing rapidly with the temperature. Above 1150°, the oxide is completely decomposed, the metal being obtained. The oxide, Rh_2O_3, is greyish-black. The previously recorded formation of lower oxides is due to incomplete oxidation.

C. H. D.

The Oxides of Ruthenium. A. GUTBIER [with G. A. LEUCHS and H. WIESSMANN] (*Zeitsch. anorg. Chem.*, 1916, **95**, 177—187. Compare A., 1905, ii, 534).—Ruthenium tetroxide reacts explosively with even very dilute alcohol. By using dilute aqueous solutions and taking only small quantities for each operation, a brown or black colloidal product may be obtained which may be evaporated on the water-bath. The residue does not yield constant figures either for water or oxygen. Heating in air or oxygen forms the dioxide, RuO_2. Alcohol and potassium ruthenate also yield an indefinite product, and similar mixtures are obtained from hydrogen ruthenichloride and alkali hydroxide, and from potassium ruthenate and nitric acid. C. H. D.

The Action of Selenic Acid on Osmium. KARL HRADECKY (*Österr. Chem. Zeit.*, [2], **20**, 43; from *Chem. Zentr.*, 1917, i, 949).—Cold selenic acid has no appreciable action on osmium; at about 120°, however, the metal is dissolved to a colourless solution which contains selenious acid and osmium tetroxide, but no selenate. H. W.

Mineralogical Chemistry.

Occurrence of Native Copper in the Komandor Islands, Bering Sea. J. MOROZEWICZ (*Mem. Com. Geol. Russ.*, 1912, **72**; from *Zeitsch. Kryst. Min.*, 1915, **55**, 200—202).—Two occurrences on Copper Island are described in detail. Both are in basalt-tuff, one with associated quartz and calcite, and the other with zeolites and a small amount of calcite. The copper was the last mineral to be deposited. It is chemically pure. Staronka found by the gravimetric method 99·77, and by the electrolytic method 100% Cu. The zeolites include analcite (anal. I by Staronka), and the new species, stellerite (Morozewicz, 1909).

Zeolites are also described from volcanic-tuff débris from Rechaya Bay. Analyses by Janczewsky of II, analcite (D 2·175), and III, laumontite. The latter in a moist atmosphere or under

water contains 15·26% H_2O, corresponding with the formula $CaAl_2Si_4O_{12},4H_2O$.

	SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	55·06	23·08	—	—	14·11	8·43	100·68
II.	57·40	15·55	8·38	0·46	—	18·66	100·45
III.	52·45	22·35	12·32	0·40	—	13·79	101·31

L. J. S.

Mineralogy of the Island of Borneo. G. P. TSCHERNIK (*Trav. Mus. Géol. Pierre le Grand Acad. Sci. St. Pétersbourg*, 1912, **6**, 49—95; from *Zeitsch. Kryst. Min.*, 1915, **55**, 184—191).—Material is described and analysed from the alluvial occurrences of platinum, osmiridium, and gold with associated diamond and other heavy minerals in the Tanah-Laut district, south-east Borneo. Ten analyses of platinum, which occurs usually as minute scales, show: Pt, 58·30—77·08; Ir, 3·06—28·87; Pd, 0·23—1·00; Rh, 0·21—3·86; Os, traces—1·78; Ru, traces—1·25; Fe, 4·19—10·83 (and in ferroplatinum 20·89); Cu, 0·22—1·19; Au, traces—3·70; Ag, traces—0·27; sp. gr. 16·68—22·12 (for the ferroplatinum 14·15). Fifteen analyses of osmiridium show: Ir, 10—70; Os, 17—80; Pt, 0·1—5; Rh, 1—11·25; Ru, traces—8·9; Pd, traces; Fe, traces—0·45; Cu, traces—0·51; sp. gr., 14·25—21·26. Twelve analyses of gold dust show Au, 62·06—90·99; Ag, 2·13—16·11; Cu, 0·03—5·32; Fe, trace—0·55; also traces of Bi, Hg, and sometimes small amounts of Pt, Ir, Pd. A gold amalgam, D 15·439, from near Pleiari gave: Au, 34·23; Hg, 60·57; Ag, 4·78; Pt, 0·12; chromite?, 0·09; total, 99·79, agreeing with the formula $2Au_2Hg_3 + AgHg$.

Analyses of the heavy minerals include: Rutile (anal. I), small crystal fragments. Topaz (II), transparent, pale yellow. Ilmenite (III), rounded grains. Chromite (IV), brownish-black grains. Ruby (V), rose-red grains, usually cloudy. Zircon, colourless crystals (VI) and brown crystals (VII).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.
I.	0·04	96·82	—	1·84	—	trace
II.	29·23	—	61·69	—	—	—
III.	0·43	44·02	0·11	16·06	35·83	0·53
IV.	0·43	—	9·05	14·29	12·99	—
V.	—	—	99·32	0·88	—	—
VI.	33·04	—	—	0·02	—	—
VII.	34·52	trace	—	1·26	—	—

	CaO.	MgO.		Total.	Sp. gr.
I.	—	—	[Nb_2O_5 (and Ta_2O_5) 0·42]	99·12	4·51
II.	—	—	[F, 13·72 :K_2O,Na_2O, not det.]	98·86	3·54
III.	0·08	1·98		99·04	4·62
IV.	0·40	7·37	[Cr_2O_3, 54·59]	99·12	4·68
V.	—	—		100·20	3·96
VI.	trace	—	[ZrO_2, 66·14]	99·20	4·79
VII.	—	trace	[ZrO_2, 63·31]	99·09	4·56

L. J. S.

Pyrargyrite from Nagybánya, Hungary. J. LOCZKA (*Ann. hist.-natur. Mus. Nat. Hungar.*, 1911, **9**, 318—320, 320—323; from *Zeitsch. Kryst. Min.*, 1914, **54**, 185).—Analysis gave:

Ag.	Cu.	Fe.	Sb.	As.	S.	Total.	Sp. gr.
59·82	0·07	0·12	22·00	0·08	17·82	99·91	5·852

L. J. S.

Minerals from Monte Arco, Elba, Italy. E. MANASSE (*Atti Soc. Toscana Sci. Nat. Mem.*, 1912, **28**, 118—189; from *Zeitsch. Kryst. Min.*, 1915, **55**, 315—319).—A description is given of the veins of iron, manganese, lead, and copper ores and of the surrounding rocks at Monte Arco, on the east coast of the island of Elba. Thirty mineral species are described in detail; analyses are given of the following: Pyrrhotite, massive, with lamellar to granular structure, D 4·56; Fe, 59·02; S, 39·33; CaO,MgO, traces; insol. in HCl, 0·61; total, 99·56; formula Fe_5S_6. Mispickel, massive, with lamellar structure, D 5·78; Fe, 33·28; Co, 0·48; As, 46·98; S, 18·74; insol. in HNO_3, 1·49; total, 100·97. Galena, lamellar and zinciferous; PbS, 96·45; ZnS, 3·55%. Opal associated with limonite and coloured red by iron; SiO_2, 90·88; H_2O, 4·86; Fe_2O_3, 4·14; total, 99·88. Reddish-yellow, ochreous limonite contains only 12·86% H_2O, whilst the black, pitchy variety ("stilpnosiderite") contains H_2O, 14·20; Fe_2O_3, 83·16; SiO_2, 2·57; CaO,MgO, traces; total, 99·93, agreeing with the usual formula $H_6Fe_4O_9$. Apatite occurring in quartz-tourmaline veins, gave: CaO, 54·86; P_2O_5, 42·23; Cl, 0·31; F, 2·27; insol., 0·56; total (less O for F), 99·44. Tourmaline, blackish-brown crystals, gave the results under I, agreeing with the empirical formula

$$16SiO_2,4B_2O_3,9Al_2O_3,3FeO,4MgO,Na_2O,3H_2O,$$

or, in the form deduced by Penfield and Foote,

$$H_2Na_2Fe_3Mg_4Al_6(Al_3[BOH]_2Si_4O_{19})_4.$$

Ilvaite, as black, crystalline masses, gave II. Epidote, forming a compact epidosite encrusted with minute crystals of epidote, gave III. Hedenbergite is the most abundant iron silicate (anal. IV). Yellowish asbestos gave the results under V, agreeing with the tremolite formula.

	SiO_2.	Al_2O_3	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	36·09	34·43	n. d.	8·58	trace	0·53	5·60	0·35
II.	29·61	0·63	19·81	33·78	0·51	13·23	trace	—
III.	36·51	24·50	12·38	n. d.	—	24·34	0·45	—
IV.	48·05	1·61	n. d.	26·14	1·15	20·40	1·34	—
V.	54·65	$\underbrace{\qquad 1·59 \qquad}$		—	—	14·21	25·98	0·21

	Na_2O.	H_2O.	Total.	Sp. gr.
I.	2·09	1·93	100·00*	3·12
II.	—	2·73	100·30	3·95
III.	—	1·95	100·13	3·29
IV.	—	0·68	99·37	3·50
V.	1·19	1·92	99·75	—

* Including: B_2O_3, 10·40 by difference; F, trace.

Halloysite, white, soft, and moist, is found in the magnetite and limonite masses; on drying in the air, it hardens and acquires a soap-like appearance, and then breaks with a conchoidal fracture. It is opaque, but in water becomes almost transparent, like gelatin. Optically isotropic; D 2·16, H, 1—2. Analysis of air-dried material gave: SiO_2, 39·17; Al_2O_3, 34·20; CaO, trace; H_2O, 26·72; total, 100·09. Over sulphuric acid, it soon loses 8·94% H_2O, which is reabsorbed in a moist atmosphere. At 160° 12·66% H_2O is lost, and there is no loss between 250° and 400°. At 250° the composition of the material is the same as that of kaolin, $H_4Al_2Si_2O_9$, which requires 13·91% H_2O. The water of halloysite held below this point is considered to be adsorbed water, the remainder being water of constitution. Comparative dehydration experiments were made with kaolin from Tolfa, Rome; over sulphuric acid, or up to a temperature of 400°, the loss amounts to only 0·95% of the total of 14·98% H_2O. Samoite occurring with Elba halloysite has the appearance of a hardened jelly and varies in colour, green, sky-blue, or white. D 2·08; H, 3. It is completely decomposed by hydrochloric acid with the separation of gelatinous silica. Analysis gave: SiO_2, 32·79; Al_2O_3, 34·59; CaO, 1·56; MgO, 0·50; CuO, trace; H_2O, 29·64; total, 99·08. The water is lost gradually and continuously over sulphuric acid and when heated, there being no break, as is the case with halloysite. The mineral is therefore regarded as a hydrogel or adsorption compound, and not a hydrated kaolin like halloysite. L. J. S.

Mineral Occurrences in the Worthington Mine, Sudbury, Ontario. T. L. WALKER (*Econ. Geol.*, 1915, **10**, 536—542; from *Jahrb. Min.*, 1917, i, 151—152).—The ore of this mine occurs in a somewhat weathered hornblende-plagioclase-rock, and consists mainly of pyrrhotite and copper-pyrites. Embedded in it are cleavable phenocrysts, up to 5 cm. across, of pentlandite, together with nickeliferous pyrites and small amounts of polydymite, blende, niccolite, and molybdenite. Analysis I of this pentlandite leads to the formula $(Ni,Fe)_{11}S_{10}$, already deduced by Dickson. Rounded masses of pentlandite also occur in the massive pyrites, giving the ore the appearance of a conglomerate. Analysis II of this pentlandite, D 4·638, suggests that the material is mixed with a small amount of polydymite. Analysis of the pyrites gave III.

	Fe.	Ni.	Co.	Cu.	S.	CaO.	Insol.	Total.
I.	30·68	34·48	1·28	—	32·74	—	0·56	99·74
II.	27·64	32·13	0·90	0·30	34·82	1·58	0·78	98·15
III.	44·57	2·44	—	—	51·83	—	—	98·84

The author believes that this ore has not been formed by magmatic differentiation alone, but that aqueous agencies have also played a part. L. J. S.

Chemical and Mineralogical Observations. G. A. KOENIG (*J. Acad. Nat. Sci. Philadelphia*, 1912, **15**, 405; from *Zeitsch. Kryst. Min.*, 1916, **55**, 409—410).—*Aurobismuthinite*, a new

species from unknown locality, is light grey, soft, massive, and granular with numerous cleavage surfaces; analysis: Bi, 69·50; Au, 12·27; Ag, 2·32; S, 15·35; total, 99·44, gives the formula $(Bi,Au,Ag_2)_5S_6$.

Stibiobismuthinite from Nacozari, Sonora, Mexico, as aggregates of long, prismatic crystals with the usual cleavage and polysynthetic structure of bismuthinite, gave: Bi, 69·90; Sb, 8·12; S [diff.], 21·92%, agreeing with $(Bi,Sb)_4S_7$.

Crystalline seladonite from a basalt-tuff near Vail, Arizona, consists of minute prisms, pyramids, or scales. It is bluish in the air and pale olive-green under water. Analysis under I gives the formula $(K_2,H_2,Mg,Fe)_3(Fe_2,Al_2)(SiO_3)_6,1{\cdot}24H_2O$.

	SiO_2.	SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.
I.	54·73	—	7·56	13·44	5·30	0·00
II.	—	30·47	—	50·94	—	—

	MgO.	K_2O.	Na_2O.	H_2O.	Insol.	Total.
I.	5·76	7·40	—	6·40	—	100·59
II.	—	2·02	4·20	11·73	0·69	100·01

Natrojarosite (anal. II) from a new locality, namely, San Toy Mine, Santa Eulalia, Chihuahua, Mexico, occurs with gypsum and mimetite as straw-yellow, silky aggregates of hexagonal crystals. The honey-yellow crystals of mimetite from this locality gave: PbO, 67·6; As_2O_5, 22·6; $PbCl_2$, 9·8%. L. J. S.

Chemical Constitution of Bauxite from Bihar, Hungary. B. VON HORVÁTH (*Földtani Közlöny*, 1911, **41**, 254—257, 341—343; from *Zeitsch. Kryst. Min.*, 1914, **54**, 182—183).—The bauxite deposits of the Bihar Mountains in comitat Bihar are situated on a plateau of Upper Jurassic limestone. Analyses I and II are of reddish-brown material from the neighbourhood of Vaskoh, and III of greyish-white material from Mt. Kuku, near Tizfalu. Twelve other partial analyses of the reddish-brown bauxite gave: SiO_2, 0·92—2·23; Al_2O_3, 39·32—58·60; and another partial analysis of the greyish-white gave: SiO_2, 5·55; Al_2O_3, 52·11.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	1·52	3·10	53·20	27·66	0·20	trace	14·39	100·07
II.	1·52	1·95	58·26	30·22	—	0·09	8·09	100·13
III.	12·38	3·95	58·74	7·84	0·32	0·11	16·31	99·65

L. J. S.

Mineralogy of the Kyshtymsk Mountains. A. W. NIKOLAEV (*Trav. Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1912, **6**, 171—231; from *Zeitsch. Kryst. Min.*, 1915, **55**, 182—184).—Descriptions are given of twelve mineral species and analyses of the following: Magnetite (I), granular, from Mt. Fominna. Titanomagnetite (II), as sand in the Motshalin stream. Oncosine (III, by D. S. Beljankin), resembling agalmatolite, from Borsowka. Cerolite (IV), forming the cement of a weathered serpentine "conglomerate" from the Lakejev ravine. At 125° half of the water

(9·80%) is lost. Under the microscope a gradual passage from the serpentine into the cerolite can be traced.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	0·42	0·17	—	96·74		—	—	—	—	—	97·74*
II.	1·25	4·82	5·56	68·79	19·52	—	—	—	—	—	100·78†
III.	37·42	—	38·91	1·64	—	3·31	3·55	4·88	1·24	9·00§	99·95
IV.	45·05	—	—	0·34	—	5·11	29·74	—	—	18·17	99·93‡

* Including: S, 0·003; P, 0·41; Cu, traces. † Including: MnO, 0·84. § Including: H_2O at 110°, 1·79. ‡ Including: CO_2, 1·08; SO_3, 0·44.

L. J. S.

Microchemical Reactions of Dolomite from Kielce, Poland. St. J. Thugutt (*Kosmos, Lemberg*, 1911, 409—417; from *Zeitsch. Kryst. Min.*, 1914, **54**, 198—199).—Eight analyses, by W. Koziorowski, of the Upper Devonian dolomites from various localities in govt. Kielce gave the extreme values under I. The ratio of $CaCO_3 : MgCO_3$ is 1 : 1, the excess of calcium present in some being due to the presence of calcite as proved by Lemberg's colour reactions with silver nitrate and potassium chromate or iron-alum. The Triassic dolomite of Suchedniow (anal. II, by W. Koziorowski) contains some aragonite. Other materials examined were: III, magnesite, from Ekaterinburg, Urals; IV, breunnerite, from Pfitsch, Tyrol; V, sideroplesite, from Heizenberg, Zell, Salzburg; VI, brown-spar, from Traversella, Piedmont; VII, colourless dolomite crystals, from Szabra, Ekaterinburg; VIII, dolomite crystals, from Snarum, Norway; IX, dolomite crystals, from Greiner, Tyrol; X, dolomite crystals, from Zabkowite, Moravia.

	CO_2	Al_2O_3.	FeO.	MnO.
I.	42·11—47·42	0·04—0·49	0·54—1·35	0·17—0·36
II.	40·32	1·26	2·17	1·04
III.	49·72	—	8·16	—
IV.	49·63	—	12·42	—
V.	40·82	—	43·29	—
VI.	44·47	—	11·41	—
VII.	47·07	—	2·57	—
VIII.	46·84	—	3·86	—
IX.	46·76	—	1·97	—
X.	47·49	—	1·79	0·25

	CaO.	MgO.	Insol.	Total.
I.	26·55—31·52	18·33—20·59	0·38—10·69	—
II.	26·88	15·68	13·13	100·48
III.	0·18	40·99	1·56	100·61
IV.	—	38·15	0·27	100·47
V.	—	12·89	3·00	100·00
VI.	27·55	13·99	2·73	100·15
VII.	29·89	20·38	—	99·91
VIII.	30·53	18·45	0·31	99·99
IX.	29·69	20·94	1·13	100·94
X.	30·03	20·84	0·05	100·45

Dolomite and magnesite, when well crystallised and containing iron, do not react with silver nitrate or iron-ammonium sulphate solution, but the Polish dolomites poor in iron give a distinct reaction at 100°. The dolomites from govt. Kielce show a strong

thermoluminescence at 153° with a fine red colour. Dolomite from Fassa, Tyrol, shows a red luminescence, and calcite from Seiseralpe gives out a white light at 118—132°. L. J. S.

Malachite. Formation of Pseudomorphs. R. ED. LIESEGANG (*Zeitsch. Kryst. Min.*, 1915, **55**, 264—270).—A connexion is suggested between the well-formed pseudomorphs of malachite after other minerals (cuprite, copper-glance, chessylite, etc.), and the mamillated forms so characteristic of this species. When a cube of rock-salt is placed in a concentrated solution of silver nitrate, the sodium is replaced by silver without any disturbance of the external form of the crystal. When, however, a weaker solution is employed, the surface of the cube of replaced material becomes rounded; and this rounding and irregularity of the surface increases with the greater dilution of the solution. It is therefore suggested that the mamillated forms of malachite are of pseudomorphic origin. L. J. S.

Apatite from Sunk, Styria. O. GROSSPIETSCH (*Zeitsch. Kryst. Min.*, 1914, **54**, 461—466).—Tabular crystals of apatite, transparent with a pale brownish tinge, occur in dolomite veins in a magnesite quarry at Sunk, near Trieben. $a:c=1:0.73341$. D 3·2057. Analysis shows it to be a very pure fluor-apatite, $CaF_2,Ca_4(PO_4)_3$, but the results agree equally well with the formula

$$4[3CaO(PO_4)_2,CaF_2]+3CaO(PO_4)_2,CaO,$$

representing a mixture of fluor-apatite and voelckerite. It is noted that many analyses of apatite give a total of more than 100%, which may be due to the presence of oxygen. Optical determinations are also given:

P_2O_5.	CaO.	MgO.	FeO.	CO_2.	F.	Ign.	Insol.	Total.
41·95	55·59	trace	0·08	present	3·02	0·23	0·02	100·89

L. J. S.

Mineralogy of Phosphorite Deposits. II. J. V. SAMOILOV (*Geol. Untersuch. Phosphoritlagerstätten, Moscow*, 1912, **4**, 651—671; from *Zeitsch. Kryst. Min.*, 1915, **55**, 192—193).—Experiments with plants show a difference for the phosphorites from the Gault formation as compared with those of other geological periods. Gault phosphorites from the governments Simbirsk, Saratov, and Penza, when digested with water for an hour, yielded 0·03—0·06% P_2O_5 in solution. By repeated digestion, 0·53% P_2O_5 passed into solution. Phosphorites from other geological formations do not show this reaction, nor do the Gault phosphorites from govt. Moscow and the Mangyshlak peninsula. The following are analyses by N. I. Chervyakov of Gault phosphorites from, I, Sengilei, govt. Simbirsk, and, II, from the Krutezky ravine:

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.
I.	33·42	4·85	2·29	0·62	28·24	1·19	1·43	1·40
II.	36·15	1·60	1·29	0·56	32·52	1·30	0·56	0·38

	P_2O_5.	CO_2.	F.	SO_3.	FeS_2.	Organic matter.	H_2O >110°.	Total (less O for F).
I.	18·21	2·40	1·68	1·48	1·55	0·69	1·91	100·65
II.	19·88	2·89	1·49	1·27	0·71	0·68	0·75	101·40

These analyses correspond with:

	$Ca_3(PO_4)_2$.	CaF_2.	$CaCO_3$.	$CaSO_4,2H_2O$.	Total.
I.	39·8	3·5	5·5	3·2	52·0
II.	43·2	3·1	6·6	2·7	55·6

Under the microscope the phosphate substance is seen to form the ground-mass in which are embedded quartz, glauconite, felspar, mica, pyrites, and organic remains; a later generation of radially-fibrous phosphate is also present. There is, however, nothing to suggest why a portion of the phosphate is soluble in water.

L. J. S.

Composition of Phosphorite Minerals. W. T. SCHALLER (*Bull. U.S. Geol. Survey*, 1912, **509**, 98; from *Zeitsch. Kryst. Min.*, 1916, **55**, 403).—The following formulæ are deduced from published analyses:

Dahllite	$9CaO,3P_2O_5,CaO,CO_2,H_2O$.
Francolite	$9CaO,3P_2O_5,CaF_2,CO_2,H_2O$.
Collophanite	$9CaO,3P_2O_5,CaO,CO_2,H_2O+nH_2O$.
Fluorapatite	$9CaO,3P_2O_5,CaF_2$.
Hydroxyapatite	$9CaO,3P_2O_5,CaO,H_2O$.

L. J. S.

Variscite from Sarrabus, Sardinia. A. PELLOUX (*Ann. Mus. Civ. Stor. Nat. Genova*, 1912, [iii], **5**, 470—472; from *Zeitsch. Kryst. Min.*, 1915, **55**, 314).—This mineral, not previously recorded from Italy, occurs as strings and nodules in a schistose rock at Gennarella in the commune of Villaputzo. It shows a variolitic structure and conchoidal fracture. The colour is pale green to grass-green, or yellowish in more altered specimens. D 2·47; H=4. Analysis gave:

P_2O_5.	Al_2O_3.	Fe_2O_3.	H_2O.	Total.
42·27	33·29	1·71	23·11	100·38

L. J. S.

Alunite from Marysvale, Utah. B. S. BUTLER and H. S. GALE (*Bull. U.S. Geol. Survey*, 1912, **511**, 64; from *Zeitsch. Kryst. Min.*, 1916, **55**, 403).—Alunite has recently been found as a filling in a large crevice at this locality. It is partly fine-grained with a porcellaneous aspect (anal. I), and partly coarsely crystalline with feebly translucent crystals which show a distinct cleavage (anal. II, by W. T. Schaller):

	Al_2O_3.	Fe_2O_3.	SO_3.	P_2O_5.	K_2O.	Na_2O.	H_2O (<110°).	H_2O (>110°).	SiO_2.	Total.
I.	34·40	trace	36·54	0·50	9·71	0·56	0·11	13·08	5·28	100·18
II.	37·18	trace	38·34	0·58	10·46	0·33	0·09	12·90	0·22	100·10

L. J. S.

Constitution and Genesis of Iron Sulphates. IX. Voltaite from Szomolnok, Hungary. RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1914, **54**, 127—147. Compare A., 1913, ii, 715).—A specimen from Szomolnok consists of black, crystalline

voltaite with a few pale brown grains of szomolnokite (J. A. Krenner, 1891). A microchemical analysis of the latter, made on a few milligrams by J. Donau, gave the results under I leading to the formula $FeSO_4,H_2O$. Ferropallidite from Chili (A., 1903, ii, 555) is identical with szomolnokite.

	SO_3.	Fe_2O_3.	Al_2O_3.	FeO.	ZnO.	CuO.	MgO.	NiO.	K_2O.	Na_2O.	H_2O.	Total.
I.	45·66	7·43	—	34·46	—	—	—	—	—	—	12·45	100·00
II.	46·78	13·47	1·58	14·07	1·69	0·55	0·48	0·08	4·73	0·50	15·70	99·73

The voltaite (anal. II) gives the formula $R_3''R_2'''(SO_4)_6,9H_2O$, when the K_2O is reckoned as $R''O$. This and previous analyses give the ratios for $R_2O:RO:R_2O_3:SO_3:H_2O$ between the extremes 1:2:1:8:12 and 1:6:1:8:12. The curve plotting the temperature and loss of water commences at 200° and shows a break at 270°, at which point about $7H_2O$ is lost.

An aqueous solution of the voltaite deposits crystals of metavoltine, but in the presence of free sulphuric acid sphæro-crystals and composite pseudo-cubic crystals of voltaite are deposited; of these a detailed description is given. L. J. S.

Ilsemannite, Hydrous Sulphate of Molybdenum. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1917, **7**, 417—420; *Chem. News*, 1917, **116**, 94).—The composition of this secondary molybdenum mineral, which is readily soluble in cold water to a deep blue solution, has previously been assumed to be $MoO_2,4MoO_3$. Material occurring disseminated through rock at Ouray, Utah, gave for the portion soluble in cold water:

MoO_3.	MoO_2.	FeO.	SO_3.	[Insol.]	H_2O.	Total.
2·37	trace	0·99	2·64	[90·50]	[3·50]	100·00

Deducting the iron as melanterite, these results lead to the formula $MoO_3,SO_3,5H_2O$. Examination of material from other localities also proves that the material is a sulphate, and is always associated with iron sulphate. Suggestions are made regarding the origin of ilsemannite by the alteration of molybdenite, jordisite, wulfenite, and molybdosodalite. L. J. S.

Crystallised Ferric Orthoarsenate. B. JEŽEK and A. ŠIMEK (*Rozpr. české Akad. Prag*, 1911, **20**, No. 16, 1—6; from *Zeitsch. Kryst. Min.*, 1914, **54**, 188—189).—In the Deacon process for the manufacture of chlorine, at Hruschau, in Silesia, there are formed on the clay balls numerous black, prismatic crystals with adamantine lustre of ferric orthoarsenate, $FeAsO_4$. The crystals are monoclinic with $a:b:c=0·6155:1:0·3221$; $\beta=77°8'$. Cleavage $c(001)$, perfect. D 4·32. Mean refractive index (Na), 1·78.
L. J. S.

Further Experiments on the Synthesis of Wulfenite. E. DITTLER (*Zeitsch. Kryst. Min.*, 1914, **54**, 332—342. Compare A., 1913, ii, 1063).—Attempts to prepare wulfenite ($PbMoO_4$) by

the action of a solution of lead hydrogen carbonate in water containing carbon dioxide on calcium molybdate, or by prolonged digestion of normal lead carbonate ($PbCO_3$) or lead sulphide (PbS) with a concentrated solution of an alkali molybdate, did not lead to the desired result. L. J. S.

Molecular Destruction of Kaolinite by Heat. A. M. SOKOLOV (*Ber. Tech. Inst. K. Nikolaus I*, 1913, **22**, 1—15; from *Zeitsch. Kryst. Min.*, 1915, **55**, 195—196).—Kaolinite from Gluchov was heated for periods of one to five hours at temperatures of 200—1000°, and the loss of water determined. The residue was digested for two hours with 16% hydrochloric acid, and the soluble alumina determined. The results obtained after ignition for one hour are:

Temp.	Loss of H_2O %.	Soluble Al_2O_3 %.	Molecular ratio $Al_2O_3 : H_2O$.
300°	0·72	2·12	1 : 1·91
400	0·67	2·08	1 : 2·03
600	10·49	28·46	1 : 2·14
700	11·92	32·30	1 : 2·06
800	12·99	34·66	1 : 2·12

With more prolonged heating, slightly higher results were obtained. From the residue a weak alkali solution extracts soluble silica. At 800° the kaolin molecule is completely broken down into its component oxides, and on this depends the method of Zemiatchensky for the analysis of clays. L. J. S.

Silicate Fusion Solutions. K. NEUBAUER (*Foldtani Közlöny*, 1911, **41**, 72—85, 197—205; from *Zeitsch. Kryst. Min.*, 1914, **54**, 184).—Experiments were conducted under the microscope with mixtures of leucite, orthoclase, and diopside in various proportions. Fusion began at 1190—1205°, that is, about the melting point of orthoclase (1190°), and was complete at a point near the arithmetical mean of the melting points of the three components. Crystallisation began at a temperature (1090—1170°) lower than the m. p. of any of the components. Crystals of leucite separated first, and then good crystals of diopside, which grow very rapidly. Orthoclase separated only as a glass. L. J. S.

Analyses of Venetian Minerals. E. BILLOWS (*Zeitsch. Kryst. Min.*, 1916, **55**, 389—390; from separate publication, *Padua*, 1912). —Allophane (anal. I) is found in an old lead mine on Monte Civillina. It is earthy or forms compact masses, white or brown in the interior, with a glassy sky-blue exterior crust. Analcite (II), crystals from druses in the augite-porphyrite of the Val dei Zuccanti. Heulandite (III), as red scales in druses in altered augite-porphyrite from the same locality. *Arduinite* (IV), a new mineral, previously regarded as natrolite, from the Val dei Zuccanti. It forms red, radially fibrous aggregates. The fibres give straight extinction and are optically negative; they show traces of cleavage

in the direction of their length. Analysis IV corresponds with the formula $(Na_2,Ca)AlSi_3O_8,2\frac{1}{2}H_2O$.

	SiO_2.	Al_2O_3.	Fe_2O_3+ Mn_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	28·01	37·17	1·42	0·23	—	—	32·08	100·34*	1·94
II.	54·08	20·95	1·78	0·40	1·02	14·01	7·82	100·06	2·24
III.	57·96	15·78	2·04	8·10	0·21	2·16	14·67	100·92	2·17
IV.	49·40	14·57	2·43	6·57	1·54	11·77	13·85	100·13	2·26

* Including also: Cr_2O_3, trace; ZnO, 0·79; CuO, 0·64.

L. J. S.

Microchemical Examination of Ittnerite and Scolopsite. ST. J. THUGUTT (*Sitzungsber. Warschauer Ges. Wiss.*, 1911, 79—87; from *Zeitsch. Kryst. Min.*, 1914, **54**, 197).—Colour reactions (with methylene-blue, or 10% silver nitrate solution and 20% potassium chromate solution) indicate that these doubtful minerals are mixtures of haüyne, gismondite, calcite, and pyrrhotite (or an alkali sulphoferrite). The fact that gismondite has been derived from haüyne suggests that the radicles $CaAl_2Si_3O_{10}$ and $CaAl_2O_4$ enter into its constitution. L. J. S.

Zeolites from Neubauerberg, Leipa, Bohemia. R. GÖRGEY (*Mitt. naturwiss. Ver. Univ. Wien*, 1911, **9**, 17; from *Zeitsch. Kryst. Min.*, 1914, **54**, 409).—Fine specimens of zeolites are found at this locality. The species represented are natrolite, analcite, chabazite, apophyllite, gyrolite, mesolite, thomsonite, heulandite, and phillipsite. Thomsonite is the latest formed mineral in the amygdales, and forms white, compact, asbestos-like masses; analysis by B. Mauritz gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
42·66	27·53	12·43	4·59	0·20	13·42	100·83	2.290

L. J. S.

Mineralogy of Graves Mountain, Georgia. T. L. WATSON and J. W. WATSON (*Bull. Phil. Soc. Univ. Virginia, Sci. Ser.*, 1912, **1**, 200—221; from *Zeitsch. Kryst. Min.*, 1916, **55**, 411).—Analyses are given of pyrophyllite (I), lazulite (II), and kyanite (III):

	SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	64·90	—	26·88	1·18	—	0·74	0·17	5·69	99·57	2·659
II.	6·05	38·25	33·92	—	3·99	3·12	9·08	5·83	100·24	2·958
III.	39·14	—	59·52	1·09	—	0·18	0·40	—	100·33	3·282

L. J. S.

Stilbite and Chabazite from Hungary. AL. VENDL (*Földtani Közlöny*, 1911, **41**, 70—71, 195—196; from *Zeitsch. Kryst. Min.*, 1914, **54**, 181—182).—Stilbite from Mt. Csódi, near Dunabogdány, gave I, and chabazite from Somosújfalu, comitat Nográd, gave II.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	56·21	16·01	trace	8·11	—	—	0·24	19·17	99·74
II.	49·81	18·42	trace	7·66	trace	0·10	1·22	22·32	99·53

L. J. S.

Microchemical Examination of Zeagonite. ST. J. THUGUTT (*Sitzungsber. Warschauer Gesell. Wiss.*, 1911; from *Zeitsch. Kryst. Min.*, 1914, **54**, 198).—Groth and Zambonini have regarded zeagonite as a basic and somewhat weathered phillipsite. Zeagonite from Vesuvius was found to contain 15·87% H_2O, that is, only slightly less than in normal phillipsite. In methylene iodide solution (1 : 1000 H_2O), the mineral shows a lilac colour by transmitted light and blue by reflected light. With 10% silver nitrate solution and potassium chromate it gives a faint orange coloration, which is more distinct at 100°. The reactions resemble those for phillipsite, but with slight differences. The mineral is regarded as a natural dehydration product of a phillipsite poor in silica. The zeagonite from Löbau is shown to be a mixture of phillipsite with 15—25% levynite. L. J. S.

Crystallised Montmorillonite and a Gel form of Planerite. HANS LEITMEIER (*Zeitsch. Kryst. Min.*, 1916, **55**, 353—371).—A yellow clay mineral from the Progress mine (copper, lead, and silver) in the Hermanli district, Zogora, Bulgaria, when received was a perfectly isotropic gel, but after being kept for three years it showed throughout the larger part a feeble birefringence, indicating that it had become crystalline. This is supposed to have been brought about by an increase in the size of the grain of the material. Analysis I agrees with the formula

$$Al_2Si_4O_{11},6H_2O.$$

	SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	CuO.	CaO.	MgO.	Insol.	H_2O.	Total.
I.	50·14	—	19·74	4·14	—	1·26	2·28	—	22·61	100·17
II.	0·16	29·06	30·46	0·54	3·81	—	0·18	1·49	34·07	99·77
III.	0·21	28·84	31·00	0·92	—	trace	0·36	2·55	34·78	98·66

Planerite occurs as white and blue compact masses in the manganese ore deposits of Arschitza, near Jakubeny, in Bukovina. It is colloidal and optically isotropic ($n_{Na} = 1·5167$), $H < 2$. Analysis II of the blue material gives the formula $Al_6P_4O_{19},18H_2O$. The amount of water depends on the vapour pressure, and the loss proceeds continuously with rise in temperature; the formula is therefore written $Al_6P_4O_{19},nH_2O$. At 100°, with $10H_2O$, the mineral is identical chemically with the crystallised planerite. It belongs to the wavellite type with $Al_2O_3 : P_2O_5 = 3 : 2$. Analysis III is of the white, less pure, material. This, when treated with a solution of copper ammonium sulphate, adsorbs 5·8% CuO. The copper in the blue mineral is therefore not an essential constituent, but adsorbed in the gel. Taking the copper into account, the formula for the blue mineral becomes $CuO,6Al_2O_3,4P_2O_5,40H_2O$, or at 100° with $20H_2O$. Cœruleolactite (T. Petersen, 1871) is identical with planerite (R. Hermann, 1862). L. J. S.

The Constitution of some Minerals of the Mica Group in the Light of the Stereo-Hexite-Pentite Theory. W. ASCH and D. ASCH (*Zeitsch. Kryst. Min.*, 1915, **54**, 584—586).—In accordance with his theory that orthosilicates can form isomorphous

mixtures with polysilicates, for example, trisilicates, Clarke has been led to ascribe very complex formulæ to the alumino-silicates "zinnwaldite" and cryophyllite (A., 1890, 460). According to the present authors, the same analyses employed by Clarke lead, in accordance with the hexite–pentite theory, to much simpler formulæ. Thus "zinnwaldite" appears to be derived from the aluminosilicic acid, $n\mathrm{H_2O,2(5Al_2O_3,18SiO_2)}$, by the replacement of part of the hydrogen by basic atoms and of part of the oxygen by fluorine. The composition of the mineral is expressed by the formula $\mathrm{K_{10}Li_{10}H_4Mn''Fe''_7Al_{20}Si_{36}F_{20}O_{112}}$.

Cryophyllite is found to have the composition

$$\mathrm{H_3K_4Li_5Fe''_{1\cdot5}Al_{55}Fe'''_{0\cdot5}F_6Si_{15}O_{43\cdot5}},$$

and can be regarded as a derivative of the aluminosilicic acid, $\mathrm{7\cdot5H_2O,3Al_2O_3,15SiO_2}$. Structural formulæ are given for both minerals. E. H. R.

The Limestones and Calciphyres of Candoglia, Italy. E. TACCONI (*Atti Soc. Ital. Sci. Nat.*, 1911, **50**, 55—93; from *Zeitsch. Kryst. Min.*, 1914, **54**, 388—389).—A detailed description of the rocks and minerals from this locality. A violet-blue mineral occurring with pistachio-green epidote in syenite-pegmatite is shown by the following analysis to belong to the epidote group. Its optical characters (high refractivity, feeble negative birefringence, $2V = 60$—$80°$, dispersion, $v > \rho$) suggest a ferriferous clinozoisite.

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	H_2O.	Total.
41·60	20·11	14·23	trace	20·16	1·58	1·94	99·62

L. J. S.

Uralite from Uralite-porphyrite from Pellinge, Finland. EERE MÄKINEN (*Geol. För. Förh.*, 1915, **37**, 633—638; from *Jahrb. Min.*, 1917, i, 142—143).—Pseudo-crystals of uralite (anal. I, D 3·118) isolated from uralite–porphyrite (anal. II) from Sådholmen, Pellinge, show the short, prismatic form characteristic of volcanic augite and the optical constants of hornblende; the latter being in agreement with the data of Ford, which showed a correlation with the chemical composition (A., 1914, ii, 211).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
I.	49·58	0·28	6·82	3·35	12·35	—	14·00
II.	56·06	0·92	13·97	1·41	7·59	0·09	6·95

	CaO.	Na_2O.	K_2O.	H_2O+.	H_2O-.	Total.
I.	11·68	0·33	0·28	1·45	0·50	100·62*
II.	9·48	2·06	0·63	0·56		99·72

* Also F, about 0·2%.

L. J. S.

Petrography of the Central Caucasus. K. J. TIMOFÉEV (*Ann. Géol. Min. Russie*, 1912, **14**, 170—173; from *Zeitsch. Kryst. Min.*, 1915, **55**, 203).—Porphyritic crystals of a rhombic pyroxene

in andesite-dacite from the Keli plateau gave the following results, agreeing with the formula $FeSiO_3,3MgSiO_3$. The mineral may therefore be regarded either as a bronzite rich in iron or as a hypersthene poor in iron.

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Total.
54·07	3·20	5·12	12·73	3·58	21·24	99·94

L. J. S.

Rare Californian Minerals. A. F. ROGERS (*School Mines Quart. New York*, 1912, **33**, 373—381; from *Zeitsch. Kryst. Min.*, 1916, **55**, 408).—Twenty-eight species are described. Analysis of crocidolite from Santa Clara County gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	H_2O.	Total
50·65	0·90	19·21	21·70	0·79	0·39	[4·93]	1·43	100·00

L. J. S.

Geometric Properties of Isomorphous Mixtures. Application to the Rhombic and Monoclinic Pyroxenes. A. LEDOUX (*Bull. Soc. franç. Minéral.*, 1916, **39**, 232—280; from *Chem. Zentr.*, 1917, ii, 37).—The author develops the relationship between the geometric constants, the chemical composition, and the density of substances in general, and for isomorphous mixtures of several components from the theoretical and mathematical side, and applies the theory to the rhombic and monoclinic pyroxenes. From an examination of several of the latter, the values of the molecular axes of the following theoretical silicates are deduced: $MgSiO_3$, $FeSiO_3$, $CaSiO_3$, $CaMg(SiO_3)_2$, $CaFe(SiO_3)_2$, and $LiAl(SiO_3)_2$. The data at present available are insufficient for the silicates containing manganese and for those with sesquioxides, such as aegirine. In the series enstatite–hypersthene and diopside–hedenbergit, the molecular axes increase with the molecular weight, that is, with the iron content. The molecular axes of a chemical compound differ from those of an isomorphous mixture of similar composition. The alteration of the molecular axes of a pyroxene which is caused by the addition of a certain molecule is not constant, but depends greatly on the nature of the pyroxene. One and the same molecule can cause diametrically opposite alterations when introduced into two different pyroxenes. A number of changes caused by the introduction of certain molecules into the diopside–hedenbergite series are discussed in detail. H. W.

Synthetical Experiments in the Pyroxene Group. VERA SCHUMOFF-DELEANO (*Centr. Min.*, 1917, 290—304).—Experiments were made with a view to obtain a clue towards the constitution of aluminous augite. Diopside was fused with varying amounts (4·5—17%) of alumina, and the resulting material slowly crystallised. There were formed homogeneous crystals of a pyroxene containing in solid solution up to about 15% Al_2O_3, which is not extracted by digesting the material with alkali hydroxide solution.

In the presence of more alumina, felspar, sillimanite, or spinel separates out. A fusion with the composition $MgAl_2SiO_6$ (a molecule often assumed to enter into the composition of aluminous augite) is unstable, and yields magnesia-anorthite, or above 1400° spinel and glass. Experiments with diopside and ferric oxide gave similar results, about 15% Fe_2O_3 being taken up in solid solution. When, however, alumina and ferric oxide are both present, magnetite, olivine, and felspar are formed. Hexagonal calcium metasilicate (α-$CaSiO_3$) and enstatite are also capable of taking up about 15% Al_2O_3 in solid solution. L. J. S.

Artificial Iron-Rhodonite in Slags from Elba, Italy. E. TACCONI (*Rassegna Mineraria, Metallurgia e Chim.*, 1911, **34**, No. 9; from *Zeitsch. Kryst. Min.*, 1914, **54**, 392).—Bessemer slags from Porto Ferrajo yielded brown, tabular and prismatic crystals, which the following analysis proves to be an iron-rhodonite, $(Mn,Fe)SiO_3$, with an absence of calcium and magnesium. The crystallographic constants, $a:b:c=1.07285:1:0.62127$; $\alpha=103°18'$, $\beta=108°44'8''$, $\gamma=81°39'16''$, are near to those of natural rhodonite.

SiO_2.	MnO.	FeO.	Al_2O_3.	Total.
43·32	32·30	22·41	1·76	99·79

L. J. S.

Gadolinite from the Radauthal, Harz. J. FROMME (*Centr. Min.*, 1917, 305—307).—Crystals of gadolinite occur with quartz, prehnite, and orthite (A., 1910, ii, 314) in small cavities in graphic granite. D^{15} 4·298. Analysis gave:

SiO_2.	ThO_2.	Y_2O_3.	Ce_2O_3.	$(Nd, Pr, La)_2O_3$.	Fe_2O_3.	FeO.
23·86	2·26	35·86	6·33	5·49	1·13	11·75

MnO.	CaO.	MgO.	K_2O.	Na_2O.	GlO.	Ign.	Total.
0·14	1·54	0·11	0·38	0·65	8·75	1·20	99·45

Reckoning CaO, Na_2O, etc., with the iron, and the loss on ignition with the glucinum, these results agree with the usual formula $Fe''Gl_2Y_2Si_2O_{10}$. The material is perfectly fresh, but a portion at least of the loss on ignition consists of water. L. J. S.

The Volcanic Exhalation. ALBERT BRUN (*Arch. Sci. phys. nat.*, 1917, [iv], **44**, 5—18).—An examination of the salts and fumarole products from numerous eruptions of Vesuvius during one hundred years, from Spagnuolo, Etna, Chineyro, Vulcano, Pico de Teyde, and Kilauea, and of volcanic specimens from great depths in the Pacific, and of a large number of specimens of lava from different sources. In addition to the elements already recognised, boron, lithium, and thallium are found to be present in the paroxysmal volcanic exhalation. The occurrence of these elements in the eruptive magmas is fairly general. Soluble thallium chloride was found in the ammonium salts from Vesuvius and Chineyro and in certain halites from Vesuvius. An insoluble thallium compound was found penetrating the red and violet scoriæ, more or

less altered by fumarole emanations. The sulphide of thallium and arsenic was found associated with the red crusts of realgar and orpiment from Vesuvius in 1906. The presence of thallium and lead is consdered to be a confirmation of the values for the mean density of the earth as found by astrophysicists. W. G.

The Hornblende-bearing Lavas of Etna. S. di Franco (*Atti Accad. Gioenia, Catania*, 1911, [v], **4**, No. 3, 1—12; from *Zeitsch. Kryst. Min.*, 1914, **54**, 204).—Several of the lavas of Etna contain enclosures and crystals of hornblende. At Milo these crystals measure 2—4 cm. in the direction of the vertical axis. Analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Ign.	Total.	Sp. gr.
40·10	2·05	14·71	9·60	4·83	12·13	11·64	0·78	4·07	0·58	100·49	2·97

L. J. S.

The Brahin Meteorites. L. L. Ivanov (*Ann. Géol. Min. Russie*, 1912, **13**, 72—76; from *Zeitsch. Kryst. Min.*, 1915, **55**, 164).—A meteorite found near the village of Kruki, 33—35 versts west of Brahin, in govt. Minsk, Russia, shows the typical structure of a pallasite; and the following analysis of the metallic portion (D 7·49) agrees closely with that made by Inostranzev in 1869 of the Brahin mass. It is concluded that the Kruki, Krukov, and Kuzovka meteorites all belong to the Brahin fall.

Fe.	Ni.	Co.	Mg.	Ca.	SiO_2.	S.	Insol.	Total.
88·58	8·38	1·07	1·12	trace	0·47	n.d.	9·39	100·01

L. J. S.

Olivine from the Brahin Meteorite. K. J. Timoféev (*Ann. Géol. Min. Russie*, 1912, **14**, 169; from *Zeitsch. Kryst. Min.*, 1915, **55**, 202).—Analysis of the olivine from the meteorite found near the village of Kruki, govt. Minsk, Russia, gave:

SiO_2.	Al_2O_3.	FeO.	MgO.	MnO.	Total.
39·87	0·35	11·96	47·35	—	99·53

L. J. S.

Analytical Chemistry.

p-Nitrophenol as an Indicator in Water Analysis. A. GOLDBERG (*Chem. Zeit.*, 1917, **41**, 599).—Although methyl-orange and *p*-nitrophenol are equally sensitive as indicators in estimating the acidity of natural waters, the colour change of *p*-nitrophenol renders its use more suitable in the case of turbid waters. *p*-Nitrophenol is not altered by boiling with water under pressure.

W. P. S.

[Stable Starch Solution.] POLLITZ (*Zeitsch. angew. Chem.*, 1917, **30**, i, 132).—The addition of a very small quantity of an alkali, for example, sodium hydroxide, prevents the bacterial decomposition of starch solution; the quantity of alkali necessary is too small to have any influence when the starch solution is used as an indicator in iodometric titrations. W. P. S.

A Substitute for Litmus for Use in Milk Cultures. WM. MANSFIELD CLARK and HERBERT A. LUBS (*J. Agric. Research*, 1917, **10**, 105—111).—The authors recommend the use of dibromo-*o*-cresolsulphonephthalein (compare A., 1916, ii, 570) in place of litmus or azolitmin as an indicator for following the changes in hydrogen-ion concentration of milk cultures. The new indicator is preferable to litmus in that it does not undergo reduction during sterilisation in the presence of milk; it can be used in very high dilution (0·005% in the form of its sodium salt); it is of definite composition, being a crystalline compound; if other conditions are constant, it will always produce the same coloration for the same P_H of the milk. Comparative tests were made of the two indicators, using a variety of organisms, and it was found that any change in reaction which could be observed with litmus could be followed equally well with the new indicator. Some of the difficulty experienced in reproducing a particular initial colour with either indicator is shown to be due to the changes in P_H which occur when milk is sterilised by heat. W. G.

Fallacies in Colorimetry. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1392—1398).—The author discusses the physical and chemical sources of error in colorimetry, illustrating his remarks by reference to Folin s creatinine estimation, and appending a long bibliography on the subject. J. C. W.

A Titration Flask. F. K. BEZZENBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1321).—The flask is recommended as a substitute for the ordinary weight burette. It is a conical one fitted with a ground-glass stopper, through which passes a relatively wide tube reaching nearly to the bottom of the flask and with its upper end ground to fit the exit tube from the stock reagent bottle. The tube is also provided with a ground-glass cap. The flask communicates with the exterior through a capillary tube, which also passes through the ground-glass stopper and enables the wider tube to be rinsed by slightly increasing the pressure in the flask and allowing the solution thus raised to run back. H. M. D.

Filter Flask. JOS. A. SHAW (*J. Ind. Eng. Chem.*, 1917, **9**, 793).—The flask has the form of an ordinary pear-shaped separating funnel. A side-tube is provided near the top for connecting the flask with the pump. The tap at the bottom has a wide bore, whilst the tubulure at the top is of a size suitable for taking the rubber stopper holding the stem of the filter funnel. W. P. S.

Analysis of Very Small Quantities of Gas. L. HAMBURGER and W. KOOPMAN (*Chem. Weekblad*, 1917, **14**, 742—752).—A description of a form of microgas-analysis apparatus adapted to the estimation of carbon dioxide and monoxide, hydrogen, methane, and nitrogen. A. J. W.

Granular Calcium Chloride as a Drying Agent. A. T. MCPHERSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1317—1319).—Experiments made with a view to test the efficiency of granular calcium chloride as a drying agent show that the substance which has been heated at 260—275° in a current of air dried over phosphoric oxide, may be used for the rapid removal of every weighable trace of moisture from a comparatively large volume of gas. The amount of air which can be dried efficiently decreases as the rate of passage of the air over the granular chloride increases. H. M. D.

Comparison of the Efficiency of some Common Desiccants. MARY V. DOVER and J. W. MARDEN (*J. Amer. Chem. Soc.*, 1917, **39**, 1609—1614).—The method employed by Baxter and Starkweather (A., 1916, ii, 637) for the comparison of the efficiencies of various desiccating agents, has been applied in the investigation of aluminium oxide, magnesium oxide, and cupric sulphate.

The results obtained show that aluminium oxide is a very efficient drying agent, and that the temperature at which this substance has been previously heated does not appreciably affect its capacity for absorbing moisture. A table is given showing the quantities of water contained in 1 litre of air which has been passed through a 30 cm. column of various desiccating agents at 25°. This table shows that aluminium trioxide, (Al_2O_3,xH_2O), potassium hydroxide, and resublimed phosphoric oxide are the three most efficient drying agents. H. M. D.

New Method for the Estimation of Hydrogen Peroxide. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1917, [iv], **44**, 150—152).—The method is based on the addition of a measured volume of hydrogen peroxide solution to an alkaline solution containing an excess of standard sodium arsenite. After two minutes, concentrated hydrochloric acid is added to the solution, and the unchanged arsenite is titrated with a standard solution of potassium iodate in the presence of chloroform as indicator. H. M. D.

Iodometric Estimation of Chlorine in Chlorides. GREGORY TOROSSIAN (*J. Ind. Eng. Chem.*, 1917, **9**, 751—752).—The chloride is mixed with finely powdered manganese dioxide and heated with the addition of sulphuric acid (1:1). The liberated chlorine is passed into potassium iodide solution, and the iodine which is set free is titrated with $N/10$-thiosulphate solution. The sulphuric acid used must be free from nitric acid, nitrous acid, and hydrochloric acid; fluorides, if present in the chloride, do not interfere, and their action on the glass vessels is not appreciable. W. P. S.

Volumetric Estimation of Chlorine in Foods, etc., without Formation of Ash by the Wet Method. A. WEITZEL (*Arb. K. Gesundh. Amt.*, 1917, **50**, 397—404; from *Chem. Zentr.*, 1917, i, 973—974).—Small quantities of chlorine are readily lost in the customary estimation of this substance in the ash of organic substances. Two processes are therefore described which are available for foods, etc., and do not necessitate the preparation of an ash. According to the material, decomposition is effected with nitric acid or sodium hydroxide. The examination of meat or dog biscuit is effected as follows. Air-dried meat (2 grams) or biscuit (5 grams) is heated with nitric acid (D 1·15, 20 c.c. or 50 c.c.) under reflux on the boiling-water-bath, with occasional shaking, for thirty minutes. Water (50 c.c. or 20 c.c.) is now added, and the mixture is heated over gauze to gentle boiling for fifteen minutes. The cooled liquid is treated with 10 c.c. of silver nitrate solution (1 c.c. = 0·005 gram NaCl), warmed for fifteen minutes on the steam-bath, cooled, diluted with water to 100 c.c., and filtered. The excess of silver nitrate is estimated in 50 c.c. of the filtrate by titration with ammonium thiocyanate in the presence of iron alum.

In the examination of ling and salted fish roe, 2 to 5 grams of the powdered, sieved, air-dried substance (according to the chlorine content) are heated on the steam-bath with occasional shaking during thirty minutes with potassium hydroxide solution (10%, 20—50 c.c.); after being cooled, the solution is diluted to 250 c.c. Twenty-five c.c. of this solution are mixed with nitric acid (D 1·15, 20 c.c.) and standard silver nitrate (20 c.c.), and the mixture is heated under reflux to gentle ebullition until the colour becomes pale. The cold liquid is diluted to 100 c.c., filtered, and the chlorine estimated in 50 c.c. of the filtrate. The process yields accurate results, which are slightly higher than those obtained by the usual method, because, in the latter case, small amounts of alkali chlorides are lost by volatilisation. H. W.

Estimation of Chlorides in Body Fluids. VICTOR JOHN HARDING and EDWARD H. MASON (*J. Biol. Chem.*, 1917, **31**, 55—58).—A modification of McLean and Van Slyke's method (A., 1915, ii, 573), in which the proteins of the blood are removed by copper sulphate and sodium hydroxide instead of by Merck's blood charcoal. H. W. B.

Water Analysis. IV. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 113—116. Compare A., 1916, ii, 448).—Methods are described for the detection and estimation of bromine, iodine, and arsenic in water and waste-waters. Bromine is estimated by distilling with sulphuric acid, potassium permanganate, and manganous sulphate after the bromine has been concentrated in a distillate by distilling the water with sulphuric acid, sodium chloride, and a definite quantity of permanganate. Iodine is found by decomposing the iodides with sulphuric acid and sodium nitrite, and the quantity of iodine is estimated iodometrically. For the detection of arsenic, a modification of the Gutzeit test is recommended, gold chloride being used on linen to obtain the stain. W. P. S.

Titration of Iodine with Thiosulphate. RICHARD KEMPF (*Zeitsch. angew. Chem.*, 1917, **30**, i, 71—72).—Attention is directed to the importance of avoiding the use of an excess of mineral acids in iodine solutions which have to be titrated with thiosulphate solution. This particularly applies to the titration of iodine liberated when ferric chloride solution is treated with potassium iodide. The added thiosulphate tends to be decomposed locally by the hydrochloric acid before it comes into contact with the iodine. W. P. S.

Estimation of Dissolved Oxygen in Water in the Presence of Nitrites and Organic Substances. H. NOLL (*Zeitsch. angew. Chem.*, 1917, **30**, i, 105—108).—Nitrites may be destroyed, previously to the estimation of dissolved oxygen, by treating the water with 1 c.c. of 50% carbamide solution and 1 c.c. of 25% sulphuric acid, and allowing the action to proceed for four hours; the use of 10% carbamide solution, as recommended by Lehmann and Fitzau, gives high results for the oxygen. Clarke's method (A., 1911, ii, 928) is untrustworthy, whilst Winkler's method (A., 1915, ii, 277) yields accurate results, particularly when sodium hydrogen carbonate is used to convert the manganous hydroxide into manganous carbonate. Rideal and Stewart's (A., 1901, ii, 472) method is also trustworthy. W. P. S.

Estimation of Ozone and Oxides of Nitrogen in the Atmosphere. FRANCIS LAWRY USHER and BASUR SANJIVA RAO (T., 1917, **111**, 799—809).—After a criticism of the various methods available for the estimation of ozone, nitrogen peroxide, and hydrogen peroxide in small quantities, the authors describe a method for the estimation of these substances in the air. The principle consists in the action of a standard solution of sodium nitrite in faintly alkaline solution on the gas under examination. In this way, nitrate is produced by the ozone, nitrate and nitrite by the nitrogen peroxide, and hydrogen peroxide has no action. For details as to the procedure, the original paper should be consulted. The method is sensitive to 1 part of nitrogen peroxide in 56 millions of air. J. F. S.

Estimation of Hydrogen Sulphide in Water at the Place where the Sample is Collected. G. INCZE (*Zeitsch. anal. Chem.*, 1917, **56**, 308—310).—The water is collected in a 300 c.c. flask and 3 c.c. of silver nitrate–ammonium nitrate solution (85 grams of silver nitrate and 200 grams of ammonium nitrate per 500 c.c.) are added. The contents of the flask are shaken, the precipitate then allowed to settle, and 101 c.c. of the clear liquid are drawn off, and the excess of silver is titrated with $N/50$-thiocyanate solution. In this titration, sulphide and chloride are estimated together. Another portion of the water is boiled to expel hydrogen sulphide, and the chloride is then titrated. The difference between the two titrations is multiplied by 0·0034 to give hydrogen sulphide in mg. per litre of water. W. P. S.

Use of Hydrazine Sulphate and Potassium Bromide in the Estimation of Sulphides in Ores. H. SCHEIDLER (*Chem. Zeit.*, 1917, **41**, 580).—A mixture of hydrazine sulphate and potassium bromide is an efficient substitute for stannous chloride for preventing the decomposition of hydrogen sulphide by ferric chloride. Five grams of potassium bromide and 3 grams of hydrazine sulphate are sufficient for 1 gram of roasted ore.

W. P. S.

Volumetric Estimation of Polysulphide, Monosulphide, and Thiosulphate Sulphur in Lime-Sulphur Liquids. A. WÖBER (*Chem. Zeit.*, 1917, **41**, 569—570).—The liquor is treated with an excess of mercuric chloride solution, ammonium chloride is added, and the mixture is titrated with $N/10$-sodium hydroxide solution; each c.c. of this solution is equivalent to 0·003206 gram of thiosulphate sulphur, $2CaS_2O_3 + 3HgCl_2 + 2H_2O = 2CaSO_4 + 4HCl + (2HgS{\cdot}HgCl_2)$. Another portion of the sample is heated with an excess of N-sodium hydroxide solution and hydrogen peroxide, and the excess of alkali is then titrated: $CaS_4 + 6NaOH + 13H_2O_2 = CaSO_4 + 3Na_2SO_4 + 16H_2O$; $CaS_5 + 8NaOH + 16H_2O_2 = CaSO_4 + 4Na_2SO_4 + 20H_2O$; $CaS_2O_3 + 2NaOH + 4H_2O_2 = CaSO_4 + Na_2SO_4 + 5H_2O$. Allowance is made for the thiosulphate in calculating the quantity of polysulphide sulphur. A further portion of the sample is then treated with an excess of $N/10$-iodine solution containing hydrochloric acid, and the excess is titrated with thiosulphate solution: $CaS_5 + I_2 = CaI_2 + 5S$; $CaS_2O_3 + I_2 = CaI_2 + CaS_4O_6$. This gives the quantity of monosulphide sulphur after allowance has been made for the thiosulphate. W. P. S.

Rapid Estimation of the Strength of Sulphuric Acid. H. DROOP RICHMOND and J. E. MERREYWETHER (*Analyst*, 1917, **42**, 273—274).—The method depends on the heat developed when sulphuric acid is diluted. Four hundred grams of water at about 18° are placed in a vacuum-jacketed flask provided with a stirrer and a thermometer reading to 0·01°. The temperature soon becomes constant, and is noted; 5 c.c. of the sample are then added from a pipette, the latter is allowed to drain for fifteen seconds, and the mixture is stirred until the temperature is constant. The water equivalent of the calorimeter used by the authors was 14·5 grams, and the volume of sulphuric acid delivered by the 5 c.c. pipette averaged 4·911 c.c.; from these data, and from the results recorded by Pickering (T., 1890, **57**, 64), the following formula was calculated: $\% = 100 - 7{\cdot}6(3{\cdot}994 - R)$. The results obtained agree, within 0·1%, with those found by the ordinary volumetric method. W. P. S.

Chemical Control of Ammonia Oxidation. PAUL J. FOX (*J. Ind. Eng. Chem.*, 1917, **9**, 737—743).—For the examination of the gases used and produced in the oxidation of ammonia by passing it over a heated catalyst, it is recommended that the ammonia in the mixture of ammonia and air be estimated by direct absorp-

tion in standard acid. The exit gases from the plant contain nitric oxide, water vapour, oxygen, ammonium nitrate or nitrite, and nitrogen. The gas is first mixed with an excess of oxygen, then passed through an absorption vessel containing standard alkali solution, and next through a similar vessel containing alkali solution and hydrogen peroxide. Subsequent titration of the contents of the latter vessel, using sodium alizarinsulphonate as indicator, gives the quantity of nitric oxide present. The quantity of ammonia in the gases is found by treating the neutralised contents of the second absorption vessel with sodium hypobromite and measuring the volume of the evolved nitrogen. The nitrous acid is obtained by adding a measured volume of hydrogen peroxide to the contents of the first absorption vessel and titrating the mixture with permanganate solution; the hydrogen peroxide is also titrated separately with the permanganate solution, and the quantity of nitrous acid is calculated from the difference between the two titrations. W. P. S.

Estimation of Nitrogen in Nitrates and Nitrites. TH. ARND (*Zeitsch. angew. Chem.*, 1917, **30**, i, 169—172).—Two hundred and fifty c.c. of the solution, containing about 0·05 gram of nitrogen (as nitrate or nitrite), are placed in a distillation flask and 5 c.c. of 20% magnesium chloride solution and 3 grams of finely divided copper–magnesium alloy (60% copper, 40% magnesium) are added. The mixture is distilled at once, 200 c.c. of distillate being collected in a receiver containing an excess of standard acid, and the excess is titrated in the usual way. If it is desired to work on a quantity of nitrate or nitrite equivalent to 0·1 gram of nitrogen, the amount of alloy used should be increased to 5 grams. W. P. S.

Estimation of Nitrate in Sewage by means of *o*-Tolidine. EARLE B. PHELPS and H. L. SHOUB (*J. Ind. Eng. Chem.*, 1917, **9**, 767—770).—Twenty-five c.c. of the sample are boiled for thirty seconds with 0·5 c.c. of a solution containing 5% of sodium hydroxide and 1·5% of sodium chloride, then cooled, and 1 c.c. of the clear, supernatant liquid is evaporated in a porcelain basin. To the dry residue is added 0·2 c.c. of tolidine reagent (0·4 gram of *o*-tolidine in 100 c.c. of $N/1$-hydrochloric acid) and 0·5 c.c. of concentrated sulphuric acid, run gently down the sides of the dish, but not mixed. After five minutes, the liquid is caused to run round the side of the basin, 5 c.c. of water are added, the solution is transferred to a tube, diluted to 10 c.c., and the coloration compared at once with those obtained with definite quantities of standard nitrate solution. W. P. S.

The Forerunners of Kjeldahl's Method for Estimating Nitrogen. E. SALKOWSKI (*Biochem. Zeitsch.*, 1917, **82**, 60—67).—Reference is made to a method of Heintz and Ragsky described in Hoppe-Seyler's "Handbuch der physiologisch- und pathologisch-chemischen Analyse" (1875) for the estimation of urea by conver-

sion into ammonia by sulphuric acid. Also to a paper by Grete (*Ber.*, 1878, **11**, 1598). S. B. S.

Estimation of Nitrogen in Nitro-compounds. A. P. Sachs (*J. Soc. Chem. Ind.*, 1917, **36**, 915—916).—The somewhat low results obtained by Colver and Prideaux (this vol., ii, 340) in estimating nitrotoluenes by the stannous chloride reduction method are due to incomplete reduction of the nitro-compound under the experimental conditions. With the primary object of examining nitrated solvent naphthas, the author has modified the procedure in the following manner. The sample (0·2 gram) is heated in a sealed tube at 120° for two hours with 15 c.c. of stannous chloride solution ($SnCl_2,2H_2O$, 350 grams; 25% hydrochloric acid, 700 grams). The tube should be shaken every fifteen minutes, since otherwise dark particles due to carbonisation or tarry matters are sometimes formed. After being cooled, the contents of the tube are diluted with water to 100 c.c.; portions of 10 c.c. each are titrated with $N/10$-iodine, starch being used as indicator. A blank experiment should be performed simultaneously.

The method gives excellent results with nitrobenzene, *m*-dinitrobenzene, mononitrocymene, and with certain of the nitrated 'solvent naphthas,' but the problem cannot be considered as definitely solved. When time permits, the Dumas method is found to give the more trustworthy results. H. W.

Estimation of Phosphoric Acid in Phosphate Rock. C. C. Semple (*Eng. and Min. J.*, 1917, **103**, 1140—1141; from *J. Soc. Chem. Ind.*, 1917, **36**, 933).—The sample (0·5—1 gram) is decomposed by means of nitric and hydrochloric acids, and the silica is removed by twice evaporating to dryness in the customary manner. The dry residue is treated with hydrochloric acid (10 c.c.) and, after dilution with boiling water, the solution is filtered from insoluble matter and the latter is washed until the bulk of the filtrate and washings measures 175—200 c.c. Ammonia is added with constant stirring to this filtrate until a gelatinous precipitate of calcium, iron, and aluminium phosphates commences to form; ammonia (D 0·9, 30 c.c.) is then added in excess and the whole stirred vigorously. A saturated solution of citric acid (10 c.c.) is now added, and the solution is stirred for two minutes, at the end of which time, if the precipitated phosphates have not re-dissolved, more citric acid solution is added drop by drop until the phosphate solution is clear. Magnesia mixture (30 c.c.) is now added, and the solution is stirred until the precipitate of magnesium ammonium phosphate begins to be formed; after remaining for three hours it is filtered. The volume of citric acid required to clear the solution is proportional to the amount of phosphoric acid present in the liquid and, by use of a solution of citric acid of known strength for this purpose, an approximate idea of the strength of the sample may be obtained. The results agree closely with those obtained by the molybdate method. H. W.

Volumetric Estimation of Pyrophosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **99**, 184—186).—A solution of sodium pyrophosphate, acidified with a known quantity of sulphuric or hydrochloric acid, may be titrated with sodium hydroxide, the maximum redness of phenolphthalein being taken as the end-point. The indication is sharper in presence of sodium chloride.

Sodium pyrophosphate solution may also be estimated by adding it to an excess of silver nitrate solution, collecting and washing the precipitate of silver pyrophosphate, and titrating the filtrate with thiocyanate. The silver cannot be replaced by lead.

Formulæ are given for the titration of ortho-, pyro-, and metaphosphoric acids in the same solution with sodium hydroxide, the indicators used being methyl-orange, phenolphthalein, and silver nitrate–lacmoid (compare this vol., ii, 101). C. H. D.

Applications of Gas Analysis. I. Estimation of Carbon Dioxide in Alveolar Air and Blood, and the Carbon Dioxide Combining Power of Plasma, and of Whole Blood. YANDELL HENDERSON and W. H. MORRISS (*J. Biol. Chem.*, 1917, **31**, 217—227).—Simple apparatus is described for carrying out the above measurements with tolerable accuracy sufficient for clinical use. H. W. B.

Titration of Carbonic Acid and its Salts. I. M. KOLTHOFF (*Chem. Weekblad*, 1917, **14**, 780—793; *Zeitsch. anorg. Chem.*, 1917, **100**, 143—158).—Carbon dioxide in potable water can be estimated by titrating 100 c.c. with $N/10$-alkali hydroxide and 2 drops of 1% phenolphthalein as indicator. The reaction is complete when the rose-red colour persists for five minutes.

Alkali carbonates can be accurately titrated to alkali hydrogen carbonate by adding 10 c.c. of neutral glycerol to 25 c.c. of the liquid, and 1 drop of phenolphthalein as indicator. Standard acid is then slowly added until the colour is discharged. A. J. W.

Estimation of Carbonates in Limestone and other Materials. J. F. BARKER (*J. Ind. Eng. Chem.*, 1917 **9**, 786—787).—An instrument similar to a hydrometer is used. The bulb of the instrument is divided into two parts: in the upper, concentrated hydrochloric acid is placed, whilst the limestone or other carbonate is placed in the lower part and water is added through the hollow, graduated stem until the latter, when placed in a cylinder of water, is immersed up to the zero mark. A tap connecting the two compartments of the bulb is now turned so as to admit the hydrochloric acid into the limestone chamber. As the carbon dioxide escapes through the hollow stem, the instrument rises in the water, and, when the reaction is complete, the graduation mark at the surface of the water is noted. This mark indicates the calcium carbonate content of the limestone. The stem of the instrument may be graduated so as to show directly either the calcium carbonate or carbon dioxide content of a sample. W. P. S.

Cobaltinitrite Method for the Estimation of Potassium. R. C. HAFF and E. H. SCHWARTZ (*J. Ind. Eng. Chem.*, 1917, **9**, 785—786).—The following procedure is recommended for the estimation of potassium in clinker, etc. Two grams of the sample are ground with 0·5 gram of ammonium chloride, the mixture is transferred to a platinum crucible containing a layer of calcium carbonate, another layer of calcium carbonate is placed over the mixture, and the mixture is heated strongly. After cooling, the mass is treated with water, the solution filtered, and the filtrate evaporated with the addition of an excess of acetic acid. The residue is dissolved in a small quantity of hot water, 15 c.c. of cobalt reagent (220 grams of sodium nitrite, 113 grams of cobalt acetate, and 100 c.c. of glacial acetic acid per litre) are added, and the mixture is evaporated to a pasty consistence. When cold, the precipitate is treated with 30 c.c. of cold water, collected on an asbestos filter, and washed once with cold water. The precipitate is then washed into a beaker containing an excess of *N*/5-potassium permanganate solution, the mixture is diluted to 250 c.c., heated for fifteen minutes on a water-bath, then acidified with 10 c.c. of sulphuric acid (1 : 1), a slight excess of *N*/5-oxalic acid solution is added, and, when the solution has cleared, this excess is titrated with *N*/5-permanganate solution. The amount of potassium present is calculated from the actual quantity of permanganate used. W. P. S.

Method of Ashing Organic Materials for the Estimation of Potassium. P. L. BLUMENTHAL, A. M. PETER, D. J. HEALY, and E. J. GOTT (*J. Ind. Eng. Chem.*, 1917, **9**, 753—756).—To prevent loss of potassium salts by volatilisation during incineration, the organic substance should be treated with sulphuric acid in quantity more than sufficient to just moisten the sample, and the acid mixture then burnt to a white ash. The substance may also be evaporated with the addition of sulphuric acid and nitric acid before it is ignited. To estimate the potassium in the sulphated ash, the latter is dissolved in a few c.c. of dilute hydrochloric acid, the solution filtered, and the filtrate evaporated with platinum chloride. The precipitate is collected, washed with alcohol containing 10% of concentrated hydrochloric acid, then with 80% alcohol, and next treated with 6 c.c. of 20% ammonium chloride solution saturated previously with potassium platinichloride. The precipitate is now collected on an asbestos filter, washed with 80% alcohol, dried, and weighed. After the precipitate has been dissolved from the filter with hot water, the filter is dried and re-weighed. The difference between the two weights gives the quantity of potassium platinichloride obtained. W. P. S.

Methods of Titrating Mixtures of Hydrogen Carbonate and Carbonate or of Alkali Carbonate and Hydroxide necessitating neither Weighing nor previously Titrated Solutions. J. CLARENS (*Bull. Soc. chim.*, 1917, [iv], **21**, 120—124). —The estimations are carried out by means of the ureometer previously described (compare A., 1909, ii, 826). A suitable amount of

the mixture of carbonate and hydrogen carbonate is introduced into the flask and covered with water, 1 drop of methyl-orange being added as indicator. The whole is heated in a water-bath, and when equilibrium is reached the apparatus is closed and the acid is run in from the burette until the liquid is just neutral. The volume of acid V_m is read off and the level on the manometer. A similar experiment is performed, using a solution of pure normal carbonate, in quantity such that the reading on the manometer is approximately the same as in the first case. From the volume of acid used, v_n, the volume of acid, V_n, which with the requisite amount of carbonate would have given the original reading on the manometer, is calculated. Then the percentage of metal in the mixture existing in the form of hydrogen carbonate is given by $100(V_n - V_m)/V_m$. Similarly, if a mixture of carbonate and hydroxide is being examined, the percentage of hydroxide is given by $100(V_m - V_n)/V_m$. W. G.

A New Microchemical Reaction for Calcite. ST. J. THUGUTT (*Zeitsch. Kryst. Min.*, 1914, **54**, 197; from *Sitzungsber. Warschauer Ges. Wiss.*, 1911, 38—41).—Calcite intermixed with zeolites can be recognised by the following reaction. The powdered mineral (size of grains about 0·1 mm. diam.) is heated on platinum foil over a Teclu burner for fifteen seconds, and then treated with *N*/10-cobalt nitrate. The calcite becomes coated with a thin skin of a blue basic cobalt salt, whilst the zeolites are unaffected. Removing excess of the cobalt solution and adding *N*/10-silver nitrate, the bases of the zeolites are soon replaced by silver (detected with potassium chromate), whilst the basic cobalt salt becomes black owing to the formation of $Co(OH)_3$, and this quickly reduces the silver salt, producing a deposit of metallic silver on the calcite. L. J. S.

Calcined Magnesia. A. ASTRUC (*J. Pharm. Chim.*, 1917, [vii], **16**, 65—77, 110—115).—A discussion of the methods of examination and conditions as to purity given in the French Codex for calcined magnesia. As a result of the examination of a large number of samples of this substance, the author finds that none of the samples analysed conform to the Codex, and suggests new limits of variation which would not interfere with the medicinal value of the drug. In view of the difficulties in estimating small amounts of calcium in the presence of an excess of magnesium, the author proposes a rapid "diaphanometric" method. The sample under examination is dissolved in 10% acetic acid, using 0·1 gram in 25 c.c. of acid, and to it are added 5 c.c. of a 6% solution of oxalic acid. The precipitate thus obtained is compared against that obtained from a similar solution from a pure magnesia to which varying quantities of a standard calcium hydroxide solution have been added, careful note being made of the rate of appearance of the opalescence and the amount of precipitate formed. W. G.

Estimation of Zinc by Schaffner's Method. V. HASSREIDTER (*Zeitsch. anal. Chem.*, 1917, **56**, 311—316).—A discussion regarding the various modifications of this method. The average results obtained are trustworthy. W. P. S.

Volumetric Estimation of Zinc. J. W. SPRINGER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 173—174).—Zinc may be titrated with ferrocyanide solution in the presence of iron and manganese if the solution containing the three metals is first boiled with the addition of bromine, then rendered ammoniacal, and titrated, while hot, with potassium ferrocyanide solution which has been standardised against pure zinc under similar conditions. Ferrous chloride solution containing acetic acid is used as an external indicator. The presence of manganese and ferric hydroxides does not interfere with the zinc–ferrocyanide reaction. W. P. S.

Electroanalysis of Zinc and Cadmium without Platinum Electrodes. J. GUZMÁN CARRANCIO and P. POCH (*Anal. Fis. Quim.*, 1917, **15**, 235—248).—An account of the estimation and separation of zinc and cadmium in acid solution and alkaline solution by Guzmán Carrancio's electrolytic method with a copper cathode and an anode of passive iron. A. J. W.

The Second Group in Qualitative Analysis. P. BRÄUER (*Zeitsch. J. physik. chem. Unterr.*, 1917, **30**, 36; from *Chem. Zentr.*, 1917, i, 1032).—A drop of a solution of mercuric sulphide in aqua regia is rubbed on aluminium foil by means of a piece of filter paper; a moderately thick layer of aluminium oxide, formed through the aluminium amalgam, is produced in a short time. H. W.

Estimation of Mercury in Galenical Preparations. HUGO WASTENSON (*Pharm. Post.*, 1917, **50**, 125—126; from *Chem. Zentr.*, 1917, i, 912—913).—The author applies in the present instance the method of destroying organic matter previously employed in analysing protein preparations containing silver (A., 1916, ii, 577). The substance (0·3—0·5 gram) is heated with concentrated sulphuric acid (10 c.c.) and nitric acid (D 1·4, 3 c.c.) until reddish-yellow vapours are not further evolved, the liquid has become clear and colourless, and the flask filled with sulphuric acid fumes. If the vapours still smell of sulphur dioxide, treatment with nitric acid (3 c.c.) is repeated. After being cooled, water (25 c.c.) is added, which is removed by evaporation. The cold solution is treated with water (15 c.c.) and potassium permanganate solution until a permanent pink coloration is produced; the latter is discharged with ferrous sulphate, the solution diluted with water (75 c.c.), and titrated with $N/10$-ammonium thiocyanate solution in the presence of ferric alum. The method is suitable for organic and inorganic preparations of the oxides of mercury, but not for such as contain the haloids. It can also be

used for estimating mercury in ointments, plasters, and pills, provided that the ointments are tolerably free from paraffins.

H. W.

Volumetric Estimation of Mercuric Oxycyanide. ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1917, **56**, 297—299).—Mercuric oxycyanide, used by surgeons as a disinfectant, particularly for the hands, may be analysed as follows. A weighed quantity of 0·3—0·4 gram of the salt is dissolved in 50 c.c. of cold water, and the liquid, after treatment with 1 gram of sodium chloride and a drop of 0·2% methyl-orange solution, titrated with $N/10$-hydrochloric acid until it turns red. After the volume of acid required is read, 2 grams of potassium iodide are added to the solution, and the yellow liquid thus obtained is again titrated with $N/10$-hydrochloric acid as before. From the two volumes of acid required, the percentages of oxycyanide and cyanide in the salt may be calculated, the reactions proceeding according to the equations: (1) $HgO,Hg(CN)_2 + 2HCl = HgCl_2 + Hg(CN)_2 + H_2O$, and (2) $Hg(CN)_2 + 4KI + 2HCl = HgK_2I_4 + 2KCl + 2HCN$. T. H. P.

The Analysis of some Aluminium Alloys. J. H. STANSBIE (*J. Soc. Chem. Ind.*, 1917, **36**, 802—803).—For the estimation of silicon, copper, and manganese, the alloy (1 gram) is dissolved in a mixture of nitric acid and sulphuric acid, hydrochloric acid being afterwards added and the whole evaporated to fuming. All the soluble matter is taken up with water and the insoluble matter collected. After ignition and weighing, the insoluble residue is heated with hydrofluoric acid, and from the loss in weight the percentage of silicon calculated. In the filtrate from the insoluble matter the copper is estimated electrolytically, and then the manganese by the bismuthate method.

In order to estimate the zinc, 2 grams of the alloy are dissolved in 10% sodium hydroxide solution, and, after filtering through a pulp filter, the zinc is deposited on a copper-coated rotating cathode. The residue on the filter is dissolved in nitric acid and the copper estimated electrolytically, thus giving a check on the first method. If lead is present, it will show as peroxide on the anode, from which it is dissolved and estimated as sulphate. If more than 1% of iron is present, the filter pulp will be dark coloured, and should be heated with hydrochloric acid and washed. In the solution from which the copper and lead have been removed, the iron and traces of aluminium are precipitated as basic acetates, the iron and aluminium then being separated in the usual way. The final filtrate contains manganese and magnesium; the manganese is removed either as the sulphide or by means of bromine and ammonia, and the magnesium then precipitated and estimated as phosphate.

An alloy containing tin can be treated directly in the usual way with nitric acid, and the tin separated as oxide.

For the estimation of nickel (method due to F. G. BELTON), 1 gram of the alloy is dissolved in 25 c.c. of 20% sodium hydroxide

solution. After dilution, the solution is filtered through a pulp filter and the residue washed with hot water and then with nitric acid (5 c.c. in 7 c.c. water). To the filtrate are added 3 c.c. of concentrated sulphuric acid, and the copper is estimated electrolytically. The solution is then diluted to 150 c.c., 10 grams of tartaric acid and 3 grams of ammonium chloride (to keep the aluminium in solution) are added, then ammonia in slight excess, and the nickel precipitated and estimated in the usual way with dimethylglyoxime. T. S. P.

Reaction of Manganese Salts. V. Macri (*Boll. chim. farm.*, 1917, **56**, 377).—When a solution containing manganese, even in very small proportion, is rendered slightly alkaline and shaken and treated successively with a few drops of alkali oxalate solution and of acetic acid, the liquid assumes a distinct and persistent rose-red colour. The reaction is rendered more sensitive if the alkaline solution is boiled and then allowed to cool before the addition of oxalate and acetic acid, and also if one or two drops of hydrogen peroxide solution are added before the liquid is made alkaline. Salts of other metals do not interfere with the reaction, although those giving coloured solutions, especially if present in marked proportion, may mask it. T. H. P.

Rapid Estimation of Manganese and Chromium in Metallurgical Products. Travers (*Compt. rend.*, 1917, **165**, 187—189).—A modification of Smith's method for the estimation of manganese by oxidation with ammonium persulphate in the presence of silver nitrate (compare A., 1905, ii, 66). For the estimation of manganese in steel, 0·2 gram of the steel is dissolved in 20 c.c. of nitric acid (D 1·1), the solution being poured into 30 c.c. of water. This solution is heated to 40—50° and 5 c.c. of $N/10$-silver nitrate and 1·5 c.c. of a saturated solution of ammonium persulphate are added. After three minutes the whole is poured into 100 c.c. of cold water and titrated with standard arsenious acid (0·65 gram of arsenious oxide per litre). This method is exact for manganese in the presence of chromium if the latter does not exceed 5—6% or if the manganese content is less than 0·15%.

For the estimation of chromium in chrome steels a similar oxidation is performed, the silver nitrate being unnecessary; a slight excess of standard arsenious acid is added, and the excess is titrated back with standard potassium permanganate. This method is applicable for chromium even in the presence of vanadium. W. G.

Analysis of Ferrum Hydrogenio Reductum. L. W. Winkler (*Zeitsch. angew. Chem.*, 1917, **30**, i, 64).—The quantity of metallic iron in this substance may be estimated approximately (within 0·5%) by simple ignition in contact with air. The increase in weight is due to the oxidation of the iron; 100 parts by weight of Fe give 142·9 parts of Fe_2O_3. W. P. S.

Separation of Nickel and Copper by means of Dimethylglyoxime. H. GROSSMANN and J. MANNHEIM (*Zeitsch. angew. Chem.*, 1917, **30**, i, 159—160).—The solution containing nickel and copper is treated with potassium sodium tartrate in quantity sufficient to keep the copper in solution when the mixture is rendered alkaline, and the nickel is precipitated by the addition of 1% alcoholic dimethylglyoxime solution and ammonia. The precipitate is collected, dissolved in hot dilute hydrochloric acid, and the nickel reprecipitated by the addition of potassium sodium tartrate, dimethylglyoxime, and a slight excess of ammonia. The copper is then precipitated as sulphide from the filtrates. W. P. S.

Apparatus for Electrometric Titration Depending on the Change of Oxidation Potential, and its Application to the Estimation of Small Quantities of Chromium in Steel. G. L. KELLEY, J. R. ADAMS, and J. A. WILEY (*J. Ind. Eng. Chem.*, 1917, **9**, 780—782).—A convenient combination of apparatus is described; it consists of a potentiometer system, motor for operating the stirrer, and burettes for the oxidising and reducing solutions. The estimation of chromium depends on the titration of chromates with ferrous sulphate, the electrometric apparatus being used for the measurements. W. P. S.

Estimation of Nitrotoluenes. E. DE W. S. COLVER and E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1917, **36**, 856).—A reply to Knecht's comments on a previous paper by the authors (this vol., ii, 340). T. S. P.

Microanalysis of Wine. II. Estimation of Alcohol. MAXIMILIAN RIPPER and FRANZ WOHACK (*Zeitsch. landw. Versuchs-Wesen Österr.*, 1917, **20**, 102—114; from *Chem. Zentr.*, 1917, ii, 83—84. Compare this vol., ii, 106).—The process is an adaptation of Zeisel's iodide method. The original must be consulted for an exact description of the apparatus and necessary manipulation. The agreement of micro-analyses among themselves and with macrochemical estimations is generally very close. The maximum mean divergence from the average amounted in forty-seven cases to 0·15% with the former and 0·11% with the latter method. Identical results are obtained when 0·05 c.c. of wine (diluted to 0·5 c.c.) is used and when 100 c.c. are employed in the macrochemical analysis. The process is adapted to wine, beer, cider, brandy, etc. Wines containing up to 12% by volume of alcohol can be immediately investigated after dilution to ten times their volume; wines richer in alcohol require greater attention and are best diluted to twenty times their volume. The liberated iodine is titrated with $N/100$-thiosulphate solution in the presence of starch. The precautions necessary in using such dilute solutions are described. H. W.

Detection of Small Quantities of Glycerol. HANS WOLFF (*Chem. Zeit.*, 1917, **41**, 608—609).—Denigès's reaction for glycerol (conversion into dihydroxyacetone) is trustworthy for the identification of this substance, but it fails to distinguish glycerol from

ethylene glycol, which is now used as a substitute for glycerol. Ethylene glycol, especially the commercial product, also yields aldehydic substances similar to acraldehyde when heated with potassium hydrogen sulphate. The refractometer, however, will differentiate glycerol from ethylene glycol; the refractometer number of ethylene glycol is less than 15, and of glycerol more than 55. W. P. S.

Estimation of Phenol in Commercial Cresylic Acid. J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842—845).—Previous methods for the estimation of phenol in tar acids (compare Masse and Leroux, A., 1916, ii, 650) have assumed that all the phenol is collected in the fraction of the tar acids distilling up to about 200°, and that the distillate at various temperatures is of constant composition. The authors' experiments show that this is by no means the case, and they have worked out a method which depends on the fact that the addition of a suitable proportion of *o*-cresol furnishes a mixture from which the whole of the phenol can be recovered in the first fractions of the distillate. The proportion of *o*-cresol to be added in an estimation is ascertained by a preliminary fractional distillation of the tar acids which have been separated from the crude cresylic acid. The volume of the cresylic acid distilling between 195° and 202° is noted, an equal volume of *o*-cresol is added to the original tar acids, and fractionation again carried out, the fraction up to 195° being collected and weighed. The freezing point of this fraction is now taken, after the addition of sufficient phenol to an aliquot portion to yield a mixture containing at least 80% of phenol. By means of the tables given by the authors, the percentage of phenol in the original sample can then be calculated.

The tables given are: Specific gravities at 15·5° of various mixtures of phenol with *o*-, *m*-, and *p*-cresol respectively; specific gravities at 15·5° of mixtures of *m*- and *o*-cresol, and of varying mixtures of phenol with *o*- and *m*-cresol and with *p*- and *m*-cresol. Boiling points of various mixtures of phenol with *o*-, *m*-, and *p*-cresol respectively, of mixtures of *o*- and *m*-cresol, and of phenol with various mixtures of *o*-, *m*-, and *p*-cresol. A table of the fractions obtained on the distillation of various mixtures of phenol and the three cresols. T. S. P.

Detection of Phenols by the Spectroscope. J. Formánek and J. Knop (*Zeitsch. anal. Chem.*, 1917, **56**, 273—298. Compare Gsell, A., 1916, ii, 584).—In certain cases, the authors have been unable to obtain results agreeing with those recorded by Gsell (*loc. cit.*), and they point out that it is necessary to have a graph of the absorption bands exhibited by the various phthaleins in order to identify the phenol from which the phthalein was prepared. The absorption spectra should also be recorded for aqueous (acid, alkaline, and neutral) and alcoholic solutions of the substances. Some phenols (naphthols, resorcinol, naphtharesorcinol, phloroglucinol, etc.) may be converted into their triphenylmethane

derivatives before examination, others into their anthraquinone derivatives. The original should be consulted for the numerical results recorded. W. P. S.

A General Method for the Detection of Phenols in Essential Oils. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1917, **5**, 11—23).—Aldehydes, ketones, and phenols give characteristic colorations with sodium arsenotungstate or arsenotungstomolybdate, and on this is based a general method for detecting the presence of these compounds in essential oils. Hydrocarbons, alcohols, and ethers do not give colorations. A. J. W.

A New Bromine Method for the Estimation of Thymol, Salicylates, and similar Compounds. H. ELION (*J. Amer. Chem. Soc.*, 1917, **39**, 1513).—A claim that Seidell's method (A., 1912, ii, 696) is in principle the same as one described by the author in 1888. J. C. W.

Separation of Phytosterol and Cholesterol (from Fats and Oils) and the Digitonin-Precipitation Method of Marcusson and Schilling. J. PRESCHER (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 481—485).—The author proposes to saponify the fat or oil by heating it with aqueous potassium hydroxide solution and potassium carbonate solution. The resulting soap is decomposed with hydrochloric acid, chloroform is added, and the chloroform solution of the fatty acids is separated, filtered, and treated at 50° with a 1% alcoholic digitonin solution. The mixture should be stirred during the precipitation with digitonin. W. P. S.

Modification of Fehling's Method for the Estimation of Sugar. KUNO WOLF (*Zeitsch. angew. Chem.*, 1917, **30**, i, 80).—Whilst the modification suggested by Lenk (see this vol., ii, 341) introduces certain errors in the estimation of reducing sugars, these are not of such magnitude as to interfere with the usefulness of the method for the estimation of sugar in urine.

W. P. S.

Estimation of Sugars. EUSEBIO LÓPEZ (*Anal. Fis. Quim.*, 1917, **15**, 248—251).—A modification of Fehling's method of sugar estimation, employing potassium cyanide. It is applicable to the estimation of dextrose, invert-sugar, maltose, and lactose.

A. J. W.

Estimation of Sugar. N. SCHOORL and I. M. KOLTHOFF (*Pharm. Weekblad*, 1917, **54**, 949—953).—A review of methods of estimating sugar in which the use of potassium iodide is avoided or the amount of the salt required is small. A. J. W.

Rapid and Accurate Method of Estimating Dextrose. JAMES BURMANN (*Schweiz. Apoth. Zeit.*, 1917, **55**, 196—199; from *Chem. Zentr.*, 1917, ii, 84).—The method is intended mainly for

the analysis of urine, and avoids complex apparatus by using a normal drop counter and a graduated test-tube. The Fehling's solution is of such concentration that 2 c.c. = 0·01 gram dextrose. Two c.c. of this solution are heated to boiling and the urine added drop by drop from the drop counter, with constant heating of the mixture, until the blue colour just disappears and the yellow coloration (action of alkali on sugar) is formed. Per cent. dextrose = number of drops used : 200. If the change of colour occurs before the fifth drop is added, the urine should be suitably diluted.

H. W.

Estimation of Dextrose in Muscular Tissue. RALPH HOAGLAND (*J. Biol. Chem.*, 1917, **31**, 67—77).—The muscular tissue is extracted with boiling water and the extract treated with excess of phosphotungstic acid. After filtration, and removal of the excess of phosphotungstic acid by means of potassium chloride, the dextrose in the filtrate is estimated in the usual way. The author claims that this procedure removes creatinine and all reducing substances other than dextrose from the muscle extract.

H. W. B.

***o*-Tolylhydrazine, a new Characteristic and Sensitive Reagent for *d*-Galactose.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1917, **37**, 108—110).—With *o*-tolylhydrazine in alcoholic solution, *d*-galactose gives an *o-tolylhydrazone*, colourless needles, m. p. 176°, after warming on a water-bath for half an hour. Neither *l*-arabinose, xylose, rhamnose, fucose, dextrose, mannose, nor lævulose gives a hydrazone with *o*-tolylhydrazine even on evaporation. With this reagent, 10 parts of *d*-galactose, with 5 parts of each of the other above-mentioned sugars, dissolved in 40 parts of water, give the characteristic, crystalline hydrazone.

W. G.

Estimation of Starch in Clover. TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1917, **8**, 55—56; from *Chem. Zentr.*, 1917, i, 1151—1152).—The author has recently described a direct method for the estimation of starch (this vol., ii, 342). In certain cases, particularly with ground clover, difficulties are experienced in the precipitation of the starch, due to the action of protective colloids; in such cases, the following modification of the process is advocated. The substance (1 gram) is dissolved in 20 or 25 c.c. of calcium chloride solution (1 : 1); the solution is diluted to 100 c.c. and immediately filtered, since otherwise a larger amount of the disturbing substance is dissolved. Seventy-five c.c. of the filtrate are treated with a slight excess of *N*/50-iodine solution and agitated for five minutes. The residue is extracted with dilute calcium chloride solution (1 in 10; 30—40 c.c.), *N*/50-thiosulphate solution is added until it is decolorised, and the starch is again precipitated and centrifugalised; the residue is treated with a few c.c. of dilute calcium chloride solution containing a few

drops of iodine solution, filtered through a Gooch crucible, and washed with calcium chloride solution containing iodine. The process is completed as described in the previous communication.

H. W.

[**Estimation of Pectin- and Lignin-Methyl Alcohol in Roots.**] TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1917, **8**, 1—29; from *Chem. Zentr.*, 1917, i, 1154—1155).—See this vol., i, 616.

The Inadequacy of the Basic Ferric Acetate Test for Acetates. LOUIS J. CURTMAN and BEN R. HARRIS (*J. Amer. Chem. Soc.*, 1917, **39**, 1315—1317).—Systematic observations have been made with a view to devise a definite procedure for the detection and approximate estimation of acetates by the formation of basic ferric acetate. The results show that this is not sufficiently sensitive for general use in the detection of acetates, and that it does not afford an approximate method for estimating the quantity of acetate present in a given solution.

H. M. D.

Rapid Process for the Estimation of the Higher Fatty Acids and Soaps in Fæces. JOHN SMITH SHARPE (*Biochem. J.*, 1917, **11**, 96—100).—For the estimation of the total fatty acids, including those combined as neutral fats and soaps, as well as those present in the free state, 1 gram of the thoroughly mixed material is boiled for fifteen minutes with 50 c.c. of a 2% alcoholic potassium hydroxide solution. After cooling, the solution is made up to 200 c.c. and filtered. Of the filtrate, 2 c.c. or 5 c.c., depending on the quantity of fatty acid present, are mixed with 5 c.c. of hydrochloric acid and diluted to 50 c.c. with water. A standard is prepared, as nearly as possible at the same time, by taking 2 c.c. or 4 c.c. of a standard fatty acid solution (1 c.c. = 0·0005 gram of fatty acids), made by boiling oleic acid, 50%, palmitic acid, 25%, and stearic acid, 25%, with alcoholic potassium hydroxide, and treating with hydrochloric acid in the same way as the sample. After bringing to the same volume, both solutions are allowed to remain for five minutes, and the clouds which have then developed are compared in a nephelometer (compare Kober and Graves, A., 1915, ii, 837).

The soluble sodium and potassium soaps are first extracted with water and then estimated by the method described above. The insoluble calcium and magnesium soaps are estimated indirectly by subtraction of the amount of soluble soaps from that of the total soaps, the latter being calculated from the difference between the total fatty acids as estimated above and the free fatty acids extracted by Soxhlet's method.

H. W. B.

Detection of Small Quantities of Oxalic Acid in Wine. A. A. BESSON (*Chem. Zeit.*, 1917, **41**, 642—643; *Schweiz. Apoth. Zeit.*, 1917, **55**, 81—85).—The following results have been obtained during an investigation of the method of Kreis and Baragiola (A.,

1916, ii, 158). The relative concentration of the reagents has an influence, not only on the form of the oxalate crystals, but also on the sensitiveness of the reaction. The process is simple and trustworthy. A further simplification can be effected by the employment of stock solution prepared by dissolving crystalline calcium chloride (20 grams) in water (250 c.c.), adding acetic acid (250 c.c.), and cold, saturated sodium acetate solution (500 c.c.). Ten c.c. of this solution (filtered, if necessary) are added to 50 c.c. of wine, and the test is then performed according to Kreis and Baragiola's directions.

Oxalic acid, even in amounts as small as 0·01%, appears to exert a protective action against moulds. It has been further observed that wines which when first tested show a distinct reaction for oxalic acid, appear to be free from this substance after some weeks; the acid appears therefore to resemble malic acid in that it is gradually decomposed. H. W.

The Estimation of Succinic Acid. Egerton Charles Grey (*Bull. Soc. chim.*, 1917, [iv], **21**, 136—141; *Biochem. J.*, 1917, **11**, 134—138).—Pasteur's method for the estimation of succinic acid is satisfactory if certain precautions are taken. The concentration of the solution of the calcium salts of the mixed acids must be effected slowly in a flask with a long neck placed in an oven at a temperature just above 100°. The presence of peptone is likely to cause a large error in the results obtained for succinic acid. Glycerol causes a much smaller error, and dextrose does not interfere with the estimation. The author finds it better to estimate the total calcium and the calcium in the filtrate after the precipitation of the calcium succinate by alcohol. The amount of succinic acid present is thus arrived at by difference. W. G.

Volumetric Estimation of Zinc Phenolsulphonate. Guido Adanti (*Boll. chim. farm.*, 1917, **56**, 317—318).—In the presence of bromine and an acid, zinc phenolsulphonate reacts in accordance with the following equations: $(OH{\cdot}C_6H_4{\cdot}SO_3)_2Zn,7H_2O + H_2SO_4 = ZnSO_4,7H_2O + 2OH{\cdot}C_6H_4{\cdot}SO_3H$ and $2OH{\cdot}C_6H_4{\cdot}SO_3H + 12Br = 2C_6H_2Br_3{\cdot}OH + 6HBr$.

Exactly 0·5 gram of the crystallised zinc phenolsulphonate is dissolved in water and the solution made up to 500 c.c. In a flask holding about 300 c.c. and fitted with a ground stopper, 50 c.c. of this solution are mixed with 50 c.c. of 0·6% potassium bromide solution and 50 c.c. of 0·1671% potassium bromate solution, 5 c.c. of concentrated sulphuric acid being then added, and the flask again shaken and left closed in a dark place at about 25° for three hours. Ten c.c. of 10% potassium iodide solution, recently prepared, are next added, and, after the lapse of an hour, the iodine liberated is determined by titration with $N/10$-sodium thiosulphate. The number of c.c. of the thiosulphate used is subtracted from that required in a blank test with the 50 c.c. of bromide and 50 c.c. of bromate alone; the remainder, multiplied by 0·00447, gives the weight in grams of crystallised zinc phenolsulphonate in the 50 c.c. of solution taken. T. H. P.

Modifications of the Colorimetric Estimation of Uric Acid in Urine and in Blood. L. JEAN BOGERT (*J. Biol. Chem.*, 1917, **31**, 165—171. Compare Benedict and Hitchcock, A., 1915, ii, 602).—The author directs attention to the errors which arise in the application of the Benedict-Hitchcock-Folin method for the estimation of uric acid in urine, owing to variations in the rates of development and fading of colour in the standard and unknown solutions after the addition of the necessary reagents. They recommend that the standard solution should be left for fifteen minutes before being used in order to allow the point of maximum colour to be reached. Afterwards, allowance is made for a loss of colour at the rate of 5% per hour. The colour of the unknown solution should be measured at intervals of two to three minutes until the maximum colour has been developed.

The author also recommends the omission of the precipitation by colloidal iron in the method for the estimation of the uric acid in the blood. He states that the proteins of the blood can be sufficiently removed by treatment of the blood with dilute acetic acid and heat. H. W. B.

Estimation of Dicyanodiamide in Nitrolime. G. HAGER and J. KERN (*Zeitsch. angew. Chem.*, 1917, **30**, i, 53—54).—Five grams of the sample are shaken for some hours with 100 c.c. of 95% alcohol, the mixture is filtered, and two portions of 50 c.c. each are placed in separate beakers and diluted with about 150 c.c. of water. In one solution the cyanamide is precipitated by silver nitrate and ammonia. A few drops of sodium phosphate solution may be added to accelerate the precipitation; the precipitate is then collected, washed, and the nitrogen in it estimated by Kjeldahl's method. The other solution is treated with silver nitrate, and the mixture rendered distinctly alkaline by the addition, drop by drop, of 5% sodium hydroxide solution. The cyanamide and dicyanodiamide are thus precipitated together. The nitrogen is also estimated in this precipitate, and the difference between the amounts of nitrogen in the two precipitates gives that present as dicyanodiamide. W. P. S.

The Detection of Cryogenine in Urines. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1917, [vii], **16**, 52).—Cryogenine is readily detected in urine by the following method. To 10 c.c. of the urine are added an equal volume of water and up to 1 c.c. of a 20% solution of mercuric acetate. If the urine contains cryogenine, a characteristic, salmon-pink precipitate is formed. W. G.

Microchemical Reactions of Sparteine. O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 100—103; from *Chem. Zentr.*, 1917, i, 917—918).—A 1—2% sparteine solution immediately gives with a drop of dilute chromic acid a pale yellow precipitate consisting of small droplets, which are converted after a short time into a mass of colourless needles which speedily become straw-yellow. Single,

well-defined prisms are also formed. 0·1 mg. of the alkaloid yields after some time crystals united to form lattices, which slowly become transformed into prisms. The crystals polarise strongly and show extinction parallel to the long axis. The limit of sensitiveness is 50 μg. With concentrated zinc chloride solution (1 : 1), a white precipitate is formed which, under the microscope, is found to consist of aggregates of short rods. The crystals are colourless and shine feebly between crossed Nicols. In presence of a trace of hydrochloric acid, the white turbidity does not appear, but, after fifteen minutes, individual prismatic crystals are formed which show marked polarisation colours and extinction parallel to the long axis. Limit of sensitiveness, 0·4—0·3 μg. The reaction with silicotungstic acid is useless for microchemical purposes. When the alkaloid is warmed with copper chloride solution (4%) and hydrochloric acid, long, lemon-yellow prisms are gradually formed, which shine in all colours between crossed Nicols, have direct extinction and fairly strong pleochroism. The excess of copper chloride (which is usually only deposited when the solution is completely evaporated) appears as colourless or pale green needles or prisms. The reaction is not very sensitive. With mercuric chloride and hydrochloric acid, a white precipitate is formed, which is converted into rhombic prisms. With small amounts of alkaloid, the precipitate does not appear, but, after twenty to thirty minutes, individual prisms are formed. These polarise strongly and generally exhibit direct extinction; they are insoluble in alcohol and glycerol. Limit of sensitiveness, 30—40 μg. The reaction with zinc chloroiodide solution has been described previously (this vol., ii, 346). Hydriodic acid gives a dark brown to black precipitate; under the microscope, long, blackish-brown prisms or brown or red aggregates appear after some hours. The crystals shine red in polarised light, have extinction parallel to the long axis, and marked pleochroism. They are readily soluble in alcohol and attacked by glycerol. Limit of sensitiveness, 5—3 μg. Potassium iodide gives a brown precipitate, which is soon converted into brownish-black nodules, from which paler, prismatic needles are formed. Limit of sensitiveness, about 5 μg. Potassium bismuth iodide yields a yellow or yellowish-red precipitate unsuited to diagnosis. Potassium cadmium bromide [cadmium bromide (1 gram), potassium bromide (2 grams), water (7 grams)] yields colourless, flat prisms, which are converted into dendritic aggregates; they shine slightly grey between crossed Nicols. In addition, rhombic platelets and brown globules are formed. The crystal forms are very diverse. The crystals are insoluble in glycerol. Limit of sensitiveness, 8—5 μg. H. W.

Estimation of Theobromine. NORAH RADFORD (*née* ELLIOTT) and G. BREWER (*Analyst*, 1917, **42**, 274—276).—The theobromine is precipitated as its silver compound and the quantity of nitrogen in the latter is estimated. A weighed quantity of the sample (for example, crude theobromine) is dissolved in water and 5 c.c. of ammonia (D 0·880), the solution is boiled, and a hot

solution containing 5 grams of silver nitrate is added. The boiling is continued until the volume of the solution is reduced to about 10 c.c. The precipitate which forms is collected, washed until free from soluble silver salts, and the nitrogen in the precipitate is then estimated by Kjeldahl's method. The number of c.c. required to neutralise the ammonia produced is calculated into terms of theobromine. The presence of large quantities of caffeine does not interfere with the estimation, since this alkaloid is not precipitated under the above conditions. W. P. S.

Replacement of Acetic Acid in Chemical Investigations. THEKLA BÄCK (*Wien. Klin. Woch.*, 1917, **30**, 465; from *Chem. Zentr.*, 1917, ii, 41—42).—In the detection of albumin in urine by the potassium ferrocyanide reaction, acetic acid may be replaced by *N*/10-hydrochloric or sulphuric acid; the volume of acid used is equal to that of the urine. More concentrated acid is to be avoided. In Weber's reaction, the fæces may be treated with 20% sulphuric acid instead of glacial acetic acid until strongly acid to Congo-red; an excess or prolonged action of acid is detrimental. It is advisable to form a lower layer of guaiacum tincture and perhydrol. With acid gastric juice, the reaction does not succeed immediately, and the juice should be exactly neutralised before acidification. This applies also to fermented fæces. Hydrochloric acid is unsuitable; the fuming acid shows the reaction, but without sufficient sensitiveness. Hydrochloric acid is also less suitable than sulphuric acid in the sodium nitroprusside test for acetone. The red coloration of creatinine is stable in the presence of acetone when 25% sulphuric acid is used (it does not become cherry-red as with acetic acid), but disappears when acetone is absent. With concentrated sulphuric acid, the red coloration becomes green in the presence of acetone. H. W.

Detection of Albumin by Bleaching Powder Solution and Hydrochloric Acid. POTJAN and STEFFENHAGEN (*Deutsch. med. Woch.*, 1917, **43**, 530; from *Chem. Zentr.*, 1917, ii, 42).—A few c.c. of urine are slowly added to a mixture of bleaching powder solution (5%; 4—6 c.c.) with two drops of pure hydrochloric acid. In the presence of albumin, an immediate, blue, opalescent turbidity is produced in which the albumin, according to the quantity, is more or less densely coagulated. Less than two drops of hydrochloric acid do not ensure the complete solution of the alkaline earths. The reaction is as sensitive as the acetic acid–potassium ferrocyanide or the sulphosalicylic acid test. It can be directly applied to cloudy urine, since the opalescence or precipitate is readily recognised even in these circumstances.

H. W.

General and Physical Chemistry.

Limiting Frequency in the Spectra of Helium, Hydrogen, and Mercury in the Extreme Ultra-violet. O. W. RICHARDSON and C. B. BAZZONI (*Phil. Mag.*, 1917, [vi], **34**, 285—307).—The frequency of the shortest vibrations which are emitted by the molecules of helium, hydrogen, and mercury under the influence of electron impacts has been determined by a method of experiment which has enabled the authors to extend the ultra-violet region of observation considerably beyond the limits reached by Schumann and by Lyman. In the arrangement of apparatus, by which this extension is rendered possible, the thermionic radiation from a tungsten filament is allowed to fall on a metallic target under the influence of a measured difference of potential, and the velocity of the photoelectric electrons emitted is measured. This is effected by observing the strength of the magnetic field required to bend the path of the electrons into a circle of known radius, a method similar to that previously used by Ramsauer in investigating the velocity distribution of photo-electrons.

The results obtained for the three gases show that the helium spectrum extends to a limit which lies between $\lambda = 470$ and $\lambda = 420$ Å., and is probably near to the latter value. The hydrogen spectrum terminates at a wave-length between $\lambda = 830$ and $\lambda = 950$ Å., the limit being probably close to $\lambda\,900$. The limit of the mercury spectrum lies between $\lambda\,1000$ and $\lambda\,1200$. These limits are independent of the applied potential up to 800 volts provided that this potential exceeds a certain lower limiting value.

The observed limiting frequencies of the three spectra appear to be in satisfactory agreement with the frequencies which are calculated from Bohr's theoretical values of the ionisation potentials of the respective gases, and bear no obvious relation to the ionisation potentials determined experimentally by Franck and Hertz.

H. M. D.

Origin of the Line Spectrum Emitted by Iron Vapour in the Explosion Region of the Air-Coal-gas Flame. G. A. HEMSALECH (*Phil. Mag.*, 1917, [vi], **34**, 221—242).—In a previous paper (this vol., ii, 61), it was shown that there are two different types of iron cone lines, and experiments are now described in which the conditions governing the emission of these lines have been more fully investigated.

The changes produced in the spectrum by varying the composition of the gas mixture, by changing the atmosphere in which combustion takes place and by reversal, lead to the conclusion that nitrogen is essential for the emission of the characteristic cone spectrum of iron. It is suggested that the nitrogen combines with the iron to form a nitride, this reaction being directly responsible

for the cone lines. The formation of this nitride appears, however, to depend on the presence of oxygen in the medium surrounding the air–coal-gas flame. If ammonia is present in the air–coal-gas and oxy-coal-gas flames, the nitride is formed less readily.

When an air–coal-gas flame is heated electrically by means of a graphite rod, the intensities of the iron lines are only slightly increased. The cooling of the flame brings about a diminution in the intensities.

The behaviour of the iron lines emitted by the mantles of various flames is such as to suggest that they are largely influenced by the temperature. The absence of the supplementary iron spectrum from the cone emission of the oxy-hydrogen and oxy-acetylene flames cannot be accounted for by the higher velocity of these flames. H. M. D.

Absorption Bands of Atmospheric Ozone in the Spectra of Sun and Stars. A. Fowler and (Hon.) R. J. Strutt (*Proc. Roy. Soc.*, 1917, *A*, **93**, 577—586).—The spectrum of Sirius exhibits a group of lines near the limit of atmospheric transmission which were first described by Huggins (*ibid.*, 1890, **48**, 216). The examination of a more recent photograph of the spectrum has shown that the lines really represent a system of bands. The supposition that these bands are due to atmospheric absorption is supported by the fact that the same bands are found in the spectra of a number of stars and also in the spectrum of the low sun.

A comparison of the bands with those found in the spectrum of ozone, which has been re-examined in this connexion, shows that the atmospheric constituent responsible for the production of these bands in the solar and stellar spectra is undoubtedly ozone.

H. M. D.

Absorption Spectra of Substances containing Conjugated and Unconjugated Systems of Triple Bonds. Alexander Killen Macbeth and Alfred Walter Stewart (T., 1917, **111**, 829—841).—The fact that the absorptive power of saturated substances is less than that of the corresponding ethylenic derivatives, and that conjugation of double bonds in diethylene derivatives is accompanied by an increase in the absorptive power, has led the authors to inquire whether a similar relation obtains in the case of acetylenic derivatives.

Acetylenic compounds belonging to both aliphatic and aromatic series were examined, but the absorption spectra show that there is no close parallelism between the light-absorbing capacities of acetylenic and analogous ethylenic derivatives, and that the above generalisation is not applicable to substances containing conjugated and unconjugated systems of triple bonds.

The observations afford further evidence, however, with regard to the influence which is exerted by residual affinity on the absorptive power, and an attempt is made to formulate this in general terms. H. M. D.

Effect of Additional Auxochromes on the Colour of Dyes. II. Triphenylmethane- and Azo-dyes. PRAPHULLA CHANDRA GHOSH and EDWIN ROY WATSON (T., 1917, **111**, 815—829).—The absorption bands in solutions of different concentrations were determined by observing the positions of the edges of the bands with an ordinary spectroscope, as in the previous investigation of the xanthene and anthraquinone groups of dyes (T., 1915, **107**, 1581; 1916, **109**, 544).

In some cases, the multiplication of auxochromes has but little influence on the position of the bands, the only effect observed being a strengthening and broadening of the bands. In other cases, the bands are shifted to a considerable extent, but remain of about the same breadth, whilst in yet other cases additional bands make their appearance. Even in the same series, very diverse effects have been observed, and the authors conclude that more material is required before any explanation of the effects produced by multiplication of auxochromes can be attempted.

H. M. D.

Production of Coloured Flames of High Luminosity for Demonstration and Experimental Purposes. G. A. HEMSALECH (*Phil. Mag.*, 1917, [vi], **34**, 243—245).—The apparatus described affords a ready means of obtaining highly luminous, coloured flames with either the electric or Gouy sprayer, and makes use of the fact that the admixture of oxygen to the gases feeding an air–coal-gas flame greatly intensifies the flame lines. The arrangement is such that the flame can be fed in succession with the sprays from a number of different solutions without any re-adjustment of the gas mixture. H. M. D.

The Nomenclature of Radio-elements. K. FAJANS (*Zeitsch. Elektrochem.*, 1917, **23**, 250—257).—The chaotic state of radioactive nomenclature is discussed, and all the various names used for the same members of the disintegration series by different writers set forth. This is particularly confusing in the case of the branch series starting from the three C-members. It is suggested that, pending an international revision of the nomenclature, the names first used should be employed. The difference in the names in use is often slight, as, for example, in the suffixes I and II, or 1 and 2, applied to mesothorium. The following is the nomenclature, according to the principle recommended, in the cases where more than one name is in vogue: uranium I and II, uranium X_1 and X_2, mesothorium 1 and 2. For the C-members and their branch products, the parent C-member is designated C_1 in each case, whilst RaC' and RaC_2, AcC_2 and AcD, ThC_2 and ThD, are respectively the α- and the β-ray-giving products in the two branches. In symbols, the prefix "radio" is to be designated by Rd, not Ra; thus RdTh for radiothorium.

For future readjustment of the nomenclature, the suggestion is made to designate by the index l, meaning lateral, the first branch

product, and by *m*, *n*, etc., later products of the branch. Thus Ra$C_1{}^l$ would stand for what above has been termed RaC_2 (and RaC_2 for what has above been termed RaC'), and Ra$C_1{}^m$ for the still unknown product of Ra$C_1{}^l$. This is to apply to all three series, although in the actinium series Ac$C_1{}^l$ would denote the main product rather than the branch product. The almost insuperable difficulties in the way of a consistent and at the same time convenient and suggestive nomenclature are considered with great thoroughness. F. S.

The X-ray Spectra of Isotopic Elements. MANNE SIEGBAHN and W. STENSTRÖM (*Compt. rend.*, 1917, **165**, 428—429).—A comparison of the *X*-ray spectra of the isotopes, lead and radium-*G*, shows that the wave-lengths of the lines in the series *L*, and α and β in series *M*, agree to within about $0{\cdot}0001 \times 10^{-8}$ cm. for the two isotopes. W. G.

Potential of the Lead Electrode. GILBERT N. LEWIS and THOMAS B. BRIGHTON (*J. Amer. Chem. Soc.*, 1917, **39**, 1906—1912).—The electrode potential of lead has been measured in saturated solutions of lead chloride, bromide, and iodide. From the results obtained with the iodide solution, the normal potential is found to be 0·4125 against the normal calomel electrode and 0·1295 against the normal hydrogen electrode.

The saturated solution of lead iodide at 25° is 0·00165 mol. per litre, which gives $11{\cdot}9 \times 10^{-9}$ for the ionic solubility product. The ionic solubility products of lead bromide and lead chloride, which are calculated from the electrode potentials in the saturated solutions of the two haloids, differ considerably from those which are given by the usual method of deriving this quantity. H. M. D.

Dilatometer for Measuring the Absolute Dilatation of Liquids. JEAN ESCARD (*Ann. Chim. anal.*, 1917, **22**, 169).—The apparatus consists of a 1-litre copper flask enclosed in a 2-litre glass flask; the space between the walls of the two flasks holds 1 litre. The necks of the flasks are elongated, and the outer one is graduated. The liquid under examination is filled into the space between the two flasks, and the dilatation with rise of temperature is observed by the rise in the level of the liquid in the graduated neck. The cubical dilatation of the two vessels is determined before the instrument is used. W. P. S.

Fenchone in Cryoscopy. TEMISTOCLE JONA (*Gazzetta*, 1917, **47**, ii, 87—98).—The paper records the results obtained in cryoscopic investigations of thirty-two organic substances, using fenchone as the solvent. The mean value of *K* for fenchone, calculated from the results obtained with twenty-one of these substances, is 68·10. R. V. S.

The Viscosity of Liquids. II. The Viscosity–Composition Curve for Ideal Liquid Mixtures. JAMES KENDALL and KENNETH POTTER MONROE (*J. Amer. Chem. Soc.*, 1917, **39**, 1787—1802. Compare A., 1914, ii, 109).—The question of the

connexion between the viscosity and the composition of ideal binary mixtures has been examined by experiments with mixtures of benzene and benzyl benzoate, benzene and ethyl benzoate, toluene and ethyl benzoate, and of toluene and benzyl benzoate. The components of each of these pairs of liquids differ widely both with respect to viscosity and molecular weight, and the observations afford in consequence a stringent test of the various formulæ which have been put forward to express the relation between the viscosity and the composition of ideal mixtures. The data are considered more particularly with reference to the nine formulæ which result when the simple mixture rule is applied to the viscosity, fluidity, or logarithmic viscosity, and the composition expressed in terms of weight, volume, or molecules, and it is found that none of these equations is in approximate agreement with the facts. On the other hand, the results obtained for the first three pairs of liquids agree closely with those calculated from the formula $\eta^{\frac{1}{3}}=x\eta_1^{\frac{1}{3}}+(1-x)\eta_2^{\frac{1}{3}}$, in which x and $1-x$ are the molar fractions of the two components, the viscosities of which are η_1 and η_2 respectively. For mixtures of toluene and benzyl benzoate, on the other hand, the observed viscosities diverge considerably from those given by the cube root formula. H. M. D.

The Viscosity of Liquids. III. Ideal Solutions of Solids in Liquids. JAMES KENDALL and KENNETH POTTER MONROE (*J. Amer. Chem. Soc.*, 1917, **39**, 1802—1806. Compare preceding abstract).—The viscosities of mixtures of benzene and naphthalene, of benzene and diphenyl, of toluene and naphthalene, and of toluene and diphenyl have been measured at 25°, and the applicability of the cube root formula $\eta^{\frac{1}{3}}=x\eta_1^{\frac{1}{3}}+(1-x)\eta_2^{\frac{1}{3}}$ tested by calculating therefrom the viscosity η_2 of the naphthalene or diphenyl. Although the several values of η_2 for each series of mixtures are in close agreement, there is a very considerable difference between the values obtained from the benzene series of mixtures on the one hand and the toluene series on the other. Thus the mean value of η_2 for naphthalene in admixture with benzene is 0·225, whilst the toluene series of mixtures gives 0·0183 as the mean value of η_2. It may be noted, however, that the ratio of these numbers is the same for diphenyl as for naphthalene. H. M. D.

Constitution and Fundamental Properties of Solids and Liquids. II. Liquids. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1917, **39**, 1848—1906).—In a previous paper (this vol., ii, 19) the author has put forward the view that the forces acting between atoms and molecules are chemical, as distinguished from physical, in character. The forces are specific in their action, have a range which is limited to atomic distances, and act only in more or less definite directions determined by the degree of saturation of the neighbouring atoms. A distinction is made between forces which correspond with primary and secondary valence, but it is claimed that these types, both of which are strictly chemical, suffice for the explanation of cohesion,

evaporation, crystallisation, adsorption, surface tension, viscosity, and other properties of liquids.

This theory of chemical forces is further developed in the present paper and applied to a series of observations which have been made on the properties of liquid surfaces.

The experiments made by Rayleigh, Marcelin, and Devaux on the spreading of oils on the surface of water have been extended. The spreading is attributed to the presence of an active group in the molecule of the oily substance, this active group having a marked affinity for water. The chemical forces which thus come into play, lead to the orientation of the oil molecules in such a way that the carboxyl groups of the molecules are all in contact or combined with water molecules, whilst the hydrocarbon chains are situated vertically above the carboxyl layer. The tendency of the oil to spread is thus attributed to the chemical forces acting between the carboxyl groups and the water molecules. It is possible to determine the cross-sections and lengths of the oriented molecules by observations of the extent to which a given weight of the oil spreads on the surface of water. Such measurements have been made for a number of substances, and it has also been found possible, by means of a special type of balance, to measure the forces which are required to compress oil films of different thicknesses. The curves obtained by plotting this force against the thickness of the film show characteristic breaks which are considered to afford confirmation of the view that the spreading of films on surfaces is determined by the configuration of the molecules and the relative activities of the different portions of the molecule.

Since adsorption is presumably a surface effect, the theory should be applicable to the explanation of phenomena which are grouped under this head. In a recent paper, Gurvich (compare A., 1914, ii, 435; 1915, ii, 744) has expressed the view that adsorption phenomena are due to physical as distinguished from chemical forces, but the author, as the result of a critical examination of the arguments put forward, arrives at the conclusion that these forces are also chemical and do not differ in any essential feature from those which give rise to the formation of typical chemical compounds. H. M. D.

The Adsorption of Carbon Dioxide and Ammonia by Charcoal. LEON B. RICHARDSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1828—1848).—The equilibrium pressures (up to 300 cm. of mercury) have been measured at temperatures between $-64°$ and $200°$ for the system charcoal–carbon dioxide, and between $-20°$ and $200°$ for the system charcoal–ammonia. At a given temperature, the adsorption is in fair agreement, over a limited range of pressures, with the equation $\alpha = a \, . \, p^{1/n}$, in which α is the volume of gas adsorbed by 1 gram of charcoal under a pressure p, a and n being constants. At higher pressures (above 60 cm.), the adsorption is less than that required by this formula, and appears to reach a maximum which at a given temperature is unchanged by further increase in the pressure. There is no evidence of a chemical action

between carbon and carbon dioxide, but at low temperatures effects are observed which suggest that part of the gas dissolves to form a solid solution. H. M. D.

The Solvent Properties of Emulsions. Theory of Dyeing in a "Boiled off Liquor" Bath. P. SISLEY (*Bull. Soc. chim.*, 1917, [iv], **21**, 155—157).—If a dilute aqueous solution of phenosafranineazonaphthol, slightly acidified with acetic acid, is gently shaken with chloroform, no emulsion being formed, the colouring matter is divided between the water and chloroform according to a definite partition-coefficient. If, however, the chloroform is emulsified, the colouring matter accumulates in the emulsified portion and the water is almost decolorised. If the tube is left, the unstable emulsion gradually breaks down and the colouring matter returns to the water. This phenomenon can be repeated indefinitely. On the basis of this, the author explains the dyeing of silk with almost insoluble dyestuffs in a "boiled off liquor" bath. A similar explanation may be given for the dyeing of cotton, using an oil emulsion as mordant, and the dyeing of leather in a fatty bath. W. G.

A Complete Review of Solutions of Oceanic Salts. I and II. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1917, **100**, 161—175, 176—236. Compare A., 1906, ii, 833; 1907, ii, 278, 480, 702). —I. The author discusses the different methods of representing graphically the solubility relations of reciprocal salt pairs, with special reference to the system $2KCl + MgSO_4 \rightleftarrows MgCl_2 + K_2SO_4$.

II. The author's graphic method of representation is applied to "doubled-ternary" systems, that is, systems comprising six different salts, as, for example, $(Na_2,K_2,Mg)(Cl_2,SO_4)$. A quantitative graphic representation has been devised for this system, in the special case of complete saturation with sodium chloride, for the range of temperature between 0° and 120°. Numerous diagrams are given, for the interpretation of which the original must be consulted. E. H. R.

The Uniform Movement of Flame in Mixtures of Acetylene and Air. WILLIAM ARTHUR HAWARD and SOSALE GARALAPURY SASTRY (T., 1917, **111**, 841—843).—Observations made in a glass tube 12 mm. in diameter show that the maximum speed is obtained with mixtures containing 8—10% of acetylene. In the curve showing the relation between the speed and the percentage of acetylene in the mixture there is a gradual flattening towards the upper and lower limits, and the crest of the curve is also flattened. Mixtures containing more than about 20% of acetylene deposit soot, and the speed of propagation of flame in such mixtures is slow. The fact that the maximum speed is found in mixtures which contain rather more than the mixture (7·75% of acetylene) which corresponds with complete combustion, is probably due to the greater thermal conductivity of acetylene as compared with air. H. M. D.

The Saponification of Fats. J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 35—63).—A mathematical discussion of the subject, in which it is shown that in the saponification of an emulsion, the reaction takes place chiefly at the boundary of the two phases, the process of saponification being governed by the value of the surface tensions between the glycerides and the saponifying medium. Equations were derived giving the relation between separated fatty acid and separated glycerol, and it was found that those equations in which the increase of concentration of the lower glycerides at the surface of contact between fat and water phase was taken into account appeared to explain the different course of the saponification in different surroundings.

W. G.

Sulphonation of Quinol. II. JOH. PINNOW (*Zeitsch. Elektrochem.*, 1917, **23**, 243—249. Compare A., 1915, i, 883).—A continuation of the previous work; the kinetics of the sulphonation of quinol have been studied at 100°, 80°, 60°, and 50° by a slightly modified method, using sulphuric acid from 7·82*M* to 13·39*M*. It is shown that if quinol is added to sulphuric acid in such quantities (1—2%) that the total volume is practically unchanged, the logarithm of the velocity of sulphonation increases proportionally to the concentration of the acid. For unit increase in the molarity of the acid, the increase in the logarithm is 0·643 at 60°, 0·612 at 80°, and 0·606 at 100°. The logarithm of the velocity for $7M H_2SO_4$ is 4·500 at 60°, $\bar{5}$·655 at 80°, and $\bar{6}$·637 at 100°. The equilibrium between quinol, quinolmonosulphonic acid, and aqueous sulphuric acid moves toward the sulphonic acid with decreasing temperature. The temperature-coefficient of the formation and hydrolysis of quinolmonosulphonic acid increases with decreasing concentration of sulphuric acid. The hydrolysis depends chiefly on the monohydrate of sulphuric acid, as was previously shown to be the case in the formation of the monosulphonic acid.

J. F. S.

The Positive Nucleus of the Atom. A. HAAS (*Physikal. Zeitsch.*, 1917, **18**, 400—402).—A theoretical paper in which the author discusses the structure of the positive nucleus with special reference to the Rutherford theory and the difficulties which are involved in the assumption that the entire mass is electromagnetic in origin. An attempt is made to meet these difficulties by a theory of atomic structure which is shown to lead directly to Moseley's formula for the connexion between the *X*-ray frequencies and the atomic numbers of the elements. H. M. D.

Problems Bearing on Residual Affinity. SPENCER UMFREVILLE PICKERING (*Proc. Roy. Soc.*, 1917, *A*, **93**, 533—549).—A theoretical paper in which the subject of residual affinity is discussed in its relation to phenomena of double decomposition and thermal data. H. M. D.

An Air-tight Gas Collecting Tube without Stopcock. GEORG WEMPE (*Zeitsch. angew. Chem.*, 1917, **30**, i, 208. Compare *ibid.*, 1914, **27**, i, 216).—The apparatus consists of a cylindrical vessel of 100—200 c.c. capacity, into which two glass tubes are fused which pass to the bottom of the vessel. The latter is completely filled with water; the gas is then admitted through one tube, the displaced water passing away through the other tube, the process being stopped while the ends of the tube still dip beneath the water. To discharge the gas, the vessel is placed in a horizontal or inclined position; water is admitted through one tube, the gas passing out through the other. H. W.

When Did the Alchemists Jan Isaac of Holland and Isaac of Holland Live? HERMANN SCHELENZ (*Zeitsch. angew. Chem.*, 1917, **30**, i, [65], 195—196).—Lippmann (A., 1916, ii, 525), in a passage from Ben Jonson's "The Alchemist," finds support for the suggestion that at the time of publication of the play, which he sets at 1610, Jan Isaac, the father, was but recently dead, whilst Isaac, the son, was still alive, and, further, that the writings of the two only appeared in print subsequently to 1600. The author objects that these conclusions are based on an imperfect translation, and that Ben Jonson's works were not printed until 1616. To judge from the authorities cited by him, Jan Isaac probably belonged to the fifteenth century—anterior to Hohenheim-Paracelsus, whom he does not mention. Jorissen (*Chem. Weekblad*, 1917, **14**, 304) states that Hugo de Groot, "Parallelon Rerum, etc.," 1602, says Jan Isaac lived 160 years before that date. Jorissen, amongst other references, also cites Lenglet du Fresnoy (1742) in favour of the view that, contrary to the usual opinion, Jan Isaac was the son of Isaac (compare also Holgen, this vol., ii, 461). T. S. PA.

Isaac of Holland and Jan Isaac of Holland. W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 897—903).—A further contribution to the discussion as to the period of these alchemists (compare preceding abstract). A. J. W.

Inorganic Chemistry.

Hydrogen Peroxide. V. Macri (*Boll. chim. farm.*, 1917, **56**, 417—418).—Hydrogen peroxide prevents the precipitation of phosphomolybdate when solutions of ammonium molybdate and phosphoric acid are mixed. Hydrogen sulphide does not affect the reaction between hydrogen peroxide and chromic acid if the chromic acid is added to the solution of hydrogen peroxide and

hydrogen sulphide. When hydrogen peroxide is treated with ammonia in presence of calcium chloride, a precipitate, CaO_2, is formed. When hydrogen peroxide is evaporated in a platinum dish in the presence of hydrogen chloride, a certain amount of chloroplatinic acid is formed.

The estimation of free acid in hydrogen peroxide may be effected by titration with permanganate, the end-point being shown by the appearance of a brownish-yellow coloration. R. V. S.

Preparation of Chlorine Gas. THE SOLVAY PROCESS Co. (U.S. Pat., 1236570, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 1048).—An alkali chloride is heated with ferric sulphate in the presence of oxygen. The ferric sulphate is formed by treating ferric oxide mixed with sodium chloride with sulphur trioxide at a temperature below that at which chlorine compounds are evolved. H. W.

Liberation of Hydrogen Sulphide from Gob Fires in Coal Mines. THOMAS JAMES DRAKELEY (T., 1917, **111**, 853—863).—According to Lewes, sulphur would be liberated in the form of sulphur dioxide if the spontaneous heating of coal was in any way connected with the presence of iron pyrites. Experiments are described which show that hydrogen sulphide is formed by passing sulphur dioxide over heated coal, by heating mixtures of coal and sulphur or mixtures of coal and iron pyrites, and by passing dry or moist hydrogen or moist carbon dioxide over heated iron pyrites. Comparison of the figures obtained in the action of dry and moist hydrogen on iron pyrites shows that the presence of water vapour favours the production of hydrogen sulphide.

In view of these observations it is improbable that the sulphur dioxide formed at the seat of a gob fire would find its way into the mine atmosphere. If not completely reduced to hydrogen sulphide by contact with heated coal in the vicinity of the fire, it would encounter hydrogen sulphide evolved by the heated material in the locality, and would thereby be reduced with the production of sulphur. H. M. D.

Action of Hydrogen on Sulphuric Acid. FRANCIS JONES (*Mem. Manchester Phil. Soc.*, 1917, **61**, No. 3, 1—3).—In the bulb of a non-tubulated retort, the open end of the neck of which dips under water, is placed some strong sulphuric acid, the remainder of the retort being filled with pure hydrogen. When the whole is left at the ordinary temperature for a few days the water gradually rises in the neck of the retort, owing to reduction of the sulphuric acid by the hydrogen with formation of sulphur dioxide (compare Milbauer, A., 1907, ii, 252). T. S. P.

Removal of Nitric Acid from Solutions of Organic Compounds. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, **31**, 599—604).—To remove nitric acid from organic mixtures the acidity of the solution is first estimated by titration of a small sample and the solution is then neutralised by means of barium

hydroxide. About 2 grams of freshly prepared aluminium amalgam are added for each gram of nitric acid and reduction of the acid allowed to proceed at the ordinary temperature for eight hours (or overnight), the solution being aerated during the entire time of reduction. The nitric acid is completely transformed into ammonia and oxides of nitrogen.

To remove the added reagents and the products of reduction, the mixture is filtered from the aluminium and mercury, and the filtrate treated with slight excess of barium hydroxide. By concentration under diminished pressure, the ammonia is removed, and the barium is then quantitatively precipitated with sulphuric acid.

The aluminium amalgam is prepared by immersing sheets of aluminium foil in a 3% solution of mercuric chloride. In a few minutes the surface of the foil is covered with mercury. The foil is immediately washed in running water and transferred at once to the nitrate solution. H. W. B.

The Melting Points of the Chlorides of Lithium, Rubidium, and Cæsium, and the Freezing Points of Binary and Ternary Mixtures of these Salts, including also Potassium and Sodium Chloride. THEODORE W. RICHARDS and W. BUELL MELDRUM (*J. Amer. Chem. Soc.*, 1917, **39**, 1816—1828).—From cooling curves the melting points obtained are lithium chloride, 613°, rubidium chloride, 714°, cæsium chloride, 645°. The lithium and cæsium chlorides were unusually pure, but the rubidium salt probably contained small quantities of impurities.

The freezing-point diagram for mixtures of potassium and lithium chloride is of the simplest type, the curves meeting at 358°. Eutectic temperatures were found for rubidium and lithium chlorides at 318° and for cæsium and lithium chlorides at 323°, but in both cases the diagram affords evidence of the existence of a 1 : 1 compound.

The freezing points of ternary mixtures of lithium and sodium chlorides with each of the three other alkali chlorides were also determined. H. M. D.

The Nature of Subsidiary Valencies. XV. Polyhaloids. FRITZ EPHRAIM (*Ber.*, 1917, **50**, 1069—1088. Compare this vol., ii, 319).—The thermal dissociation of the various alkali polyhaloids has been studied, and the temperatures determined at which the vapour pressures of the liberated halogens are equivalent to 760 mm. of mercury. The special apparatus employed is fully described, the novel feature being the device for keeping the halogen away from the mercury in the manometer.

Comparing pairs of cæsium and rubidium compounds, it is found that the ratio of the absolute temperatures of dissociation, $T_{Cs} : T_{Rb}$, is approximately constant, being about 1·12 : 1 for the whole group, and that the ratio $T : \sqrt{\text{atomic volume}}$ is the same for the two members of each series. Knowing the dissociation temperature for a given cæsium compound, it is therefore possible to

calculate the stability of the analogous rubidium compound. The tri-iodides are the most stable, and as long as one iodine atom is present, the other tri-haloids are not much less stable.

The iodine atom would thus appear to be the central atom, and it might be expected, therefore, that the compound $CsICl_2$, for example, would decompose into cæsium iodide and chlorine. As a matter of fact, it gives cæsium chloride and iodine chloride. This is not likely to be due to any secondary effect of moisture, for the purest specimens of chloride are obtained when the substance is dried over phosphoric oxide.

Calculating from the formula $T:\sqrt{v}=k$, on the basis of the rubidium and cæsium compounds, the following values for potassium salts may be obtained:

	KI_3.	KBr_3.	KI_2Br.	$KIBr_2$,	$KICl_2$.	$KClBr_2$.	$KClI_2$.
Dissoc. temp. ...	146·5°	66°	108·5°	142°	109°	47°	57°

In many cases, therefore, the dissociation temperature is below the boiling point of the ejected halogen. These compounds are unknown, and it is obvious that they are not likely to be obtained except at low temperatures.

Furthermore, the curves connecting absolute temperature and dissociation pressure for any two compounds of substances with residual affinities run parallel. For example, the ratio,

$$T_{CsBr_3} : T_{ZnCl_2,6NH_3},$$

at 200, 300, 400 . . . 700 mm. is almost constantly 1 : 1·265. The Ramsay-Young rule may therefore be employed to calculate pressures in a system of this kind when only one tension point has been determined.

The salts employed in this study were prepared by Wells and Wheeler's method, with modifications in some cases. The data recorded are the vapour pressures at different temperatures of the following salts: CsI_3, $CsBrI_2$, $CsBr_2I$, $CsCl_2I$, $CsBr_3$, $CsClBr_2$, $CsCl_2Br$, RbI_3, $RbBr_2I$, $RbBr_3$, $RbClBr_2$, $RbCl_2Br$, $RbCl_2I$, KI_3, KBr_2I, NH_4Br_2I, NH_4Br_3, NH_4Cl_2Br, and in addition cupric and chromic chlorides. J. C. W.

A Considerable Error regarding the Solubility of Calcium Carbonate in Boiling Water. ALFREDO CAVAZZI (*Gazzetta*, 1917, **47**, ii, 49—63).—When boiled with water, calcium carbonate slowly dissociates with evolution of carbon dioxide. This dissociation stops at a certain point, and is prevented if a solution of calcium hydroxide (saturated at the ordinary temperature) is added to the boiling suspension of carbonate in the proportion of about 15 c.c. per litre. After prolonged boiling of calcium carbonate in water, the substance which passes into solution is calcium hydroxide, and the amount of it depends chiefly on the volume of the liquid, the duration of the boiling, and the concentration of the solution. Small quantities of sodium carbonate (0·05 gram per litre) prevent dissociation. When calcium carbonate is produced by chemical action in aqueous solution at a low temperature, it forms supersaturated solutions even in the

presence of calcium hydroxide; the stability of these solutions depends chiefly on the concentration and the temperature

R. V. S.

Zinc Perhydrates. [Hydroperoxides.] F. W. SJÖSTRÖM (*Zeitsch. anorg. Chem.*, 1917, **100**, 237—248. Compare de Forcrand, A., 1902, ii, 322, 606; 1904, ii, 172; Kurilov, A., 1904, ii, 36; Ebler and Krause, 1911, ii, 801; Riesenfeld and Nottebohm, A., 1915, ii, 454).—When a solution of zinc sulphate is added to excess of a solution of sodium hydroxide containing hydrogen peroxide, the zinc is totally precipitated as hydroperoxide. The amount of hydrogen peroxide used cannot, however, be estimated volumetrically on account of its rapid decomposition in alkaline solution. For a more thorough examination of zinc hydroperoxide the following method of preparation was used.

Freshly ignited pure zinc oxide was left for several hours with the calculated quantity of 30% hydrogen peroxide solution at $-10°$. A product was obtained which above 2° formed a pasty mass, and when dried on a porous plate at 35—40° over soda-lime was obtained as a white powder. This was analysed by estimating active oxygen, zinc oxide, and water. It contained 8·04% active oxygen, and corresponded almost exactly with the composition $Zn_2O{<}^{O\cdot OH}_{OH}$. Towards water, alcohol, or ether at the ordinary temperature it is quite stable, and is only slowly decomposed by $2N$-sodium hydroxide. It does not appear, however, to be a simple chemical individual, since by trituration with water it can be separated into fractions containing varying quantities of active oxygen. Another preparation, fractionated in this manner before drying, gave three similar fractions, each containing about 12% of active oxygen and corresponding with no particular formula. Similar products were obtained by boiling zinc carbonate with excess of 30% hydrogen peroxide solution.

It is concluded that zinc perhydrate generally consists of a mixture of substances, derived from the two compounds $Zn(OH)_2$ and $O{<}^{Zn\cdot OH}_{Zn\cdot OH}$, the hydroperoxides being of the types $OH\cdot Zn\cdot O\cdot OH$ and $Zn(OH)\cdot O\cdot Zn\cdot O\cdot OH$. Hydrogen peroxide, since it decomposes zinc carbonate, acts as a monobasic acid. E. H. R.

Allotropy of Cadmium. FREDRICK H. GETMAN (*J. Amer. Chem. Soc.*, 1917, **39**, 1806—1816).—The results of measurements of the *E.M.F.* of cells arranged according to the scheme $Cd|CdSO_4$ solution|8% Cd amalgam would seem to indicate that there are two, and only two, allotropic modifications of cadmium between 0° and 100°. The initial value of the *E.M.F.* of such cells at 20° diminishes with time, but finally attains a constant value. When this condition has been attained, the *E.M.F.* decreases linearly with rise of temperature up to 40°.

When cells of the above type are maintained at 90°, the *E.M.F.* also becomes constant, but in this case the *E.M.F.* decreases linearly with fall of temperature down to 40°.

By means of formulæ which express the experimental observations, the temperature at which the *E.M.F.* reaches its minimum value is found to be 37·5°, which may be regarded as a close approximation to the transition temperature $Cd_\alpha \rightleftarrows Cd_\beta$. H. M. D.

Decomposition of Lead Hydrogen Arsenate by Water. C. C. McDonnell and J. J. T. Graham (*J. Amer. Chem. Soc.*, 1917, **39**, 1912—1918).—Experiments are described which show that lead hydrogen arsenate is decomposed by water with the formation of a basic salt, the reaction, which is reversible, being represented by the equation $5PbHAsO_4 + H_2O \rightleftarrows Pb_4(PbOH)(AsO_4)_3 + 2H_3AsO_4$. The concentration of arsenic acid in the equilibrium condition is very low, but if the water is continuously renewed, the lead hydrogen arsenate is completely decomposed and the residue consists of the basic lead arsenate, $Pb_4(PbOH)(AsO_4)_3,H_2O$ (hydroxy-mimetite).
H. M. D.

The Nature of Subsidiary Valencies. XVI. The Intensity of the Attachment of Water in Compounds with Water of Crystallisation. Fritz Ephraim and Paul Wagner (*Ber.*, 1917, **50**, 1088—1110).—The vapour pressures of a large number of alums and sulphates of the type

$$M_2'SO_4,M''SO_4,6H_2O,$$

have been determined at different temperatures, these salts being chosen for comparative purposes because so many of them are known, the members of one class have the same constitution, and their melting points are high. The apparatus is described.

In the case of the second class of salts, the pressures rise very slowly up to a certain point, when they increase suddenly and afterwards grow normally. This lagging effect, or "period of induction" according to Rae (T., 1916, **109**, 1229), has been reported before by Ephraim, in the case of ammines (this vol., ii, 319), and is now discussed in the light of two or three theories.

The stability of the alums is greater as the volume of the anionic metal is greater, and the same holds good for the other class (schönites), except that magnesium seems to be out of place. This is due, however, to the fact that the atom of this metal occupies less space in the double sulphate molecule than the volume as calculated from its density. The influence of the cationic metal in both series is practically nothing, but the stability of the hydrates is normally greater as the atomic volume is greater, and similarly, the change from sulphates to selenates is of very little influence on the vapour pressures. In a molecule of 48 atoms it is, of course, scarcely likely that the exchange of a single atom for a similar one will have much effect on the general stability.

The molecular volume of a stable compound is always smaller than the sum of the volumes of its decomposition products, but some elements may be relatively more compressed than others. This is seen in the case of the schönites, the necessary density data having been determined by one worker, Tutton. The double magnesium sulphates have smaller molecular volumes than the copper or manganese salts, although the atomic volume of the metal is

much greater than those of the other two. The stability of the salts is therefore more strictly parallel to their molecular volumes than to the atomic volumes of the free metals. What really matters in connexion with the stability of a compound is, therefore, not the actual contraction suffered by any particular atom during the formation of the compound, but the percentage contraction on the atomic volume, a method of calculation which has apparently only been introduced by Stephenson (*Chem. News*, 1911, **102**, 178, 187).

The data recorded refer to the following compounds: *aluminium* and *chromium* alums of K, NH_4, Rb, Cs, Na, Tl; *vanadium* alums of NH_4, Rb, Cs; *ferric* alums of NH_4, Rb, Cs; *titanium* alums of Rb, Cs; cæsium *manganic* and *cobaltic* alums; *selenate* alums of K–Al, Cs–Al, and Cs–Cr; double sulphates of K, NH_4, Rb, and Cs with Cu″, Ni″, Mg, and Mn″. J. C. W.

Martensite, Troostite, Sorbite. P. Dejean (*Compt. rend.*, 1917, **165**, 429—431. Compare this vol., ii, 477).—The author defines these three constituents of steel. For martensite he accepts Le Chatelier's definition (this vol., ii, 477). Troostite is the constituent, easily attacked by micrographic reagents, and obtained when a steel, previously heated to a temperature at least equal to that of the critical point Ac_1, is tempered with an energy insufficient to produce pure martensite. Sorbite is chemically and physically almost identical with troostite, and is obtained by thermal treatment, below the critical point Ac_1, of a steel previously tempered. It differs from troostite in its micrographic appearance. W. G.

The Heterogeneity of Steels. H. Le Chatelier and E. L. Dupuy (*Compt. rend.*, 1917, **165**, 349—352. Compare A., 1915, ii, 779).—The authors have modified the composition of Stead's reagent for characterising the heterogeneity of phosphorus steels, and have thus increased its sensitiveness and made it applicable to non-phosphorus steels. The reagent, as now prepared, contains alcohol (95%), 100 c.c.; water, 10 c.c.; crystalline copper chloride, 1 gram; picric acid, 0·5 gram; hydrochloric acid, 1·5—2·5 c.c. The proportions of copper chloride and picric acid may be varied from one-half to double the amounts given without modifying the results, but the proportions of alcohol and water must be rigorously adhered to. The exact acid content, which must be adjusted by trial, controls the success of the reagent. W. G.

Structure of Magnet Steel and its Change with Heat Treatment. Kôtarô Honda and Tahejirô Murakami (*Sci. Reports, Tôhoku Imp. Univ.*, 1917, [i], **6**, 53—70).—Four specimens of magnet steel have been investigated by thermal, magnetic, and microscopic methods. It has been found that thermal analysis is not so convenient a method for detecting minute changes in structure as is magnetic analysis. A change which is recorded by the thermal method is also easily detected by the magnetic method, and it is possible exactly to locate the transformation, but thore are

changes associated with the development or absorption of only very small amounts of heat which cannot be detected by thermal methods, whilst magnetic methods give good results.

The specimens of magnet steel gave the following analyses:

Specimen.	C.	P.	S.	Mn.	Si.	W.
Böhler	0·47	0·016	0·016	0·20	0·24	5·38
Swedish	0·59	0·015	trace	0·20	0·23	4·82
Yonago	0·61	—	—	—	0·27	4·98
Nagoya	0·36	—	—	—	0·20	6·00

The results arrived at may be summarised as follows. It is very probable that the two carbides, Fe_3C and WC, exist in magnet steels (compare Arnold and Read, *Proc. Inst. Mech. Eng.*, March 20th, 1914). These two carbides, according to the heat treatment, can exist either as a double carbide or as the separate carbides. If the specimen is heated once to 800—900° and then slowly cooled, the double carbide is formed; above the Ac_1 point the double carbide decomposes into its components, each of which dissolves in the austenite and remains as carbide up to about 900°. On heating still further, the tungsten carbide begins to dissociate, the degree of dissociation becoming almost complete at about 1100°. The carbon and tungsten formed by dissociation remain dissolved in the austenite, the carbon giving iron cementite in solid solution.

When the specimen is cooled at a normal rate from a temperature higher than 1100°, the A_1, A_2, and A_3 transformations are brought down to a much lower temperature than the A_1 point by the retarding effect of the tungsten dissolved in austenite. At about 550° the retarded A_3 transformation commences and the ferrite holding tungsten in solution separates; this separation continues over a range of about 50°, until the concentration of the solution reaches such a value that the eutectic A_1 transformation becomes possible, this taking place somewhat abruptly at about 500°, iron cementite being set free.

If the maximum temperature exceeds 1100° it is very difficult to make the two carbides combine during slow cooling; if, however, the specimen is once cooled to the ordinary temperature and then reheated to 800—900°, recombination of the two carbides takes place on cooling.

If a specimen previously heated to 1100° is kept at 700° for a sufficiently long time, the dissolved tungsten gradually takes carbon from the iron cementite to give tungsten cementite, and the A_1 transformation takes place at this temperature, showing that the effect of the tungsten is to retard the transformation. T. S. P.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphorus in Steel and Pig Iron. RICHARD FRIEDRICH (*Chem. Zeit.*, 1917, **41**, 674).—After the filtrates have been concentrated and the phosphoric acid separated as ammonium magnesium phosphate, the strongly ammoniacal liquid is treated with hydrochloric acid, added drop by drop with constant stirring, until a crystalline precipitate is no longer formed.

The precipitate of ammonium molybdate is collected after a few hours, washed with a small quantity of water, and dried between sheets of filter-paper. W. P. S.

The Chlorides and Chloro-salts of Iridium. MARCEL DELÉPINE (*Ann. Chim.*, 1917, [ix], **7**, 277—339).—A résumé of work already published (compare A., 1908, ii, 702, 765; 1910, ii, 34; 1911, ii, 806; 1914, ii, 209, 461). W. G.

Mineralogical Chemistry.

The Relations in Composition of the Different Forms of Natural Bitumens. CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1917, **39**, 2015—2027).—On distillation in a vacuum, Deerfield coal gave, in addition to gaseous products, tar, and an ammoniacal aqueous liquor, an oil which on distillation yielded fractions agreeing with the composition $C_{12}H_{24}$, $C_{10}H_{20}$, $C_{16}H_{28}$, $C_{17}H_{30}$, $C_{18}H_{32}$, $C_{20}H_{36}$, and a crystalline solid, $C_{30}H_{62}$, m. p. 60°; the composition of the fractions of general formula C_nH_{2n-4} resembles that of a large proportion of the constituents of the adjacent Mahone petroleum, and the suggestion is made that the coal represents an intermediate stage of decomposition between vegetable matter and the petroleum.

The asphaltic substance gilsonite, of Utah, on distillation gave members of the series C_nH_{2n} and C_nH_{2n-2}, resembling the same classes of hydrocarbon in petroleum; there were also obtained other unsaturated hydrocarbons, and nitrogenous organic compounds similar to those found in petroleum; these results are regarded as proof of the common origin of gilsonite and petroleum. Grahamite gave similar results to gilsonite, but the proportion of nitrogen compounds was lower, and hardly accords with the view that grahamite has been formed by the further modification of gilsonite.

D. F. T.

Glauconite or Greensand. EDWARD HART (*J. Amer. Chem. Soc.*, 1917, **39**, 1919).—Grains of marl from Mallica Hill and Sewell, New Jersey, were found to consist of a core of nearly pure silica and a covering layer of glauconite containing little or no silica. The glauconite contains Fe_2O_3, 41%; FeO, 3%; Al_2O_3, 18%; CaO, 2%; MgO, 5%; K_2O, 17%; Na_2O, 0·5%; and H_2O, 13·5%.

H. M. D.

Pisanite from Lading, Carinthia. H. LEITMEIER (*Centr. Min.*, 1917, 321—331).—The crystalline material occurs as a blue crust (anal. I) overlain by a green crust (anal. II) on limonite from

a deposit of pyrites and copper-pyrites at Lading, near St. Michael, in the Lavant valley. Apart from a small excess of water, owing to alteration, both analyses agree with the formula

$$(Cu,Fe)SO_4,7H_2O.$$

In I the ratio of copper sulphate to iron sulphate is 45 : 55, and in II it is 31 : 69.

	CuO.	FeO.	NiO.	SO_3.	H_2O.	Total.	Insol. deducted.	Sp. gr.
I.	11·67	13·43	—	28·18	46·72	100·00	1·49	1·950
II.	8·21	17·23	0·27	27·33	46·96	100·00	11·31	1·941

Published analyses of pisanite (including salvadorite) show a range in the mixed crystals of CuO 7·56—18·81 and FeO 15·85—8·51. There thus seems to be a gap at both ends of this isomorphous series; that at the iron end may be accidental, owing to lack of analyses, whilst that at the copper end is smaller than determined experimentally by Retgers (A., 1895, ii, 160). From the above density determinations and Retgers's value 1·899 for $FeSO_4,7H_2O$ (melanterite), the value 2·02 is calculated for $CuSO_4,7H_2O$, as opposed to 2·1 given by Schaller (A., 1903, ii, 490) for the natural boothite. L. J. S.

Occurrence of Euxenite in South Sherbrooke Township, Ontario. WILLET G. MILLER and CYRIL W. KNIGHT (*Amer. J. Sci.*, 1917, [iv], **44**, 243—244).—Small masses and crystals are found in the granite pegmatite of a felspar quarry near the village of Maberley. Associated minerals are pink felspar, quartz, tourmaline, mica, and pyrites. Analysis gave:

Ta_2O_5.	Cb_2O_5.	TiO_2.	ThO_2	Ce_2O_3,La_2O_3.	Y_2O_3, etc.	Fe_2O_3.	FeO.
13·89	12·73	27·70	1·34	0·62	25·64	2·63	0·51

MnO.	PbO.	U_3O_8.	CaO.	MgO.	SiO_2.	H_2O, etc.	Total.	Sp. gr.
trace	0·20	10·50	0·09	0·12	0·74	3·00	99·71	4·99

L. J. S.

Analytical Chemistry.

Treatment of Corks used in Soxhlet and other Extraction Apparatus. T. J. WARD (*Analyst*, 1917, **42**, 326—327).—Gelatin is soaked in cold water for five hours, the unabsorbed water is then decanted, the gelatin is heated until melted, and mixed with $\frac{1}{4}$ volume of glycerol and 2 volumes of water. The corks, previously bored, are immersed in this solution and heated in the same for two hours on a water-bath; they are then removed, wiped, and dried in a warm place. Corks thus treated are impervious to the vapours of ether, light petroleum, benzene, and carbon disulphide, and do not yield any extractives to these solvents. W. P. S.

Estimation of Halogens in Organic Compounds. J. F. LEMP and H. G. BRODERSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2069—2074).—A variety of organic chloro-, bromo-, and iodo-compounds have been analysed with respect to halogen by the Parr sulphur-bomb method (A., 1908, ii, 628; see also Pringsheim, A., 1904, ii, 146, 775), in which oxidation is effected with sodium peroxide. Correct results are obtainable in this way, care, however, being necessary to ensure a thorough and uniform fusion, the addition of an excess of silver nitrate to the alkaline solution obtained after the oxidation process, and the reduction of any halogen oxy-acids that may have been formed, hydrazine hydrate being the most suitable reagent for the last purpose. D. F. T.

Estimation of Chlorine in Blood Serum and other Body Fluids. M. LAUDAT (*J. Pharm. Chim.*, 1917, [vii], **16**, 168—171).—Five c.c. of the serum are mixed with 10 c.c. of $N/10$-silver nitrate solution, 6 c.c. of saturated potassium permanganate solution, and 10 c.c. of concentrated nitric acid, and the mixture is heated until a clear liquid is obtained; this requires only a few minutes. The mixture is then diluted and the excess of silver nitrate is titrated with $N/10$-thiocyanate solution, using iron alum as the indicator. W. P. S.

Modification of the McLean-Van Slyke Method for the Estimation of Chlorides in Blood. G. L. FOSTER (*J. Biol. Chem.*, 1917, **31**, 483—485. Compare McLean and Van Slyke, A., 1915, ii, 573).—The modification consists in the precipitation of the proteins of the blood by treatment with metaphosphoric acid instead of by heat and blood charcoal. H. W. B.

Identification of Chlorates in the Presence of Hypochlorites. FRITZ WISCHO (*Pharm. Post.*, 1917, **50**, 381; from *Chem. Zentr.*, 1917, ii, 133).—The following behaviour of the two substances towards brucine and hydrochloric acid can be used for the identification of sodium chlorate in the presence of sodium hypochlorite in Dakin's solution. When a solution of sodium hypochlorite (5 c.c.) of approximately the same concentration as Dakin's solution (about 0·5%) is treated with brucine hydrochloride or sulphate (0·05 gram) and dilute hydrochloric acid (5 drops), a yellow coloration is developed which becomes cherry-red when the solution is boiled; the latter coloration remains unchanged when the solution is boiled with a further 10 c.c. of dilute acid. On the other hand, a similar solution of potassium chlorate is not coloured by brucine (0·05 gram) and dilute hydrochloric acid (5 drops) in the cold; when boiled, the solution becomes yellow, and, subsequently, cherry-red, but the colour is discharged when boiling is continued after a further addition of dilute hydrochloric acid (10 c.c.). This decolorisation on subsequent boiling with much dilute hydrochloric acid is characteristic of the presence of chlorate; it also occurs when 5 c.c. of a solution containing 0·04

gram of sodium hypochlorite and 0·02 gram of potassium chlorate in water (10 c.c.) is tested as described above. H. W.

Estimation of Bromides. E. RUPP (*Arch. Pharm.*, 1917, **255**, 303—304).—The bromate method of estimating the bromide in alkali bromides or their mixtures ("bromum compositum") is modified as follows to avoid the use of hydrogen peroxide (compare this vol., ii, 327). Twenty c.c. of officinal dilute sulphuric acid, 50 c.c. of *N*/100-potassium bromate, 0·2 gram of iodine, and 0·15 gram of the bromide are diluted to 200 c.c., and the mixture is boiled after the addition of a little talc or powdered pumice until the volume has been diminished to 75 c.c. in not less than forty minutes. The mixture is cooled to the ordinary temperature, 0·5—1 gram of potassium iodide is added, and the iodine liberated by the excess of the bromate is titrated with *N*/10-thiosulphate after three to five minutes.

When the bromide is being estimated in the presence of more than about 25% of chloride, the undiluted mixture of the sulphuric acid, potassium bromate, and iodine is concentrated to about half its volume by boiling for fifteen minutes, the solution of the haloid is added, the mixture diluted to 200 c.c., and the procedure mentioned above followed. The result is 0·2—0·3 c.c. too high if the preliminary boiling is omitted. C. S.

Estimation of Selenium in Bones, Teeth, and Urine. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1917, **100**, 182—189. Compare A., 1916, i, 772).—The bones are extracted with ether, powdered, and dried at 110° to 120°, and then a weighed quantity dissolved in hydrochloric acid. After diluting with an equal volume of water, a brown precipitate containing the selenium gradually settles out. It is collected, treated with hot aqua regia, filtered, and the selenium in the filtrate precipitated as sulphide. The sulphide is then dissolved in fuming nitric acid, and silver nitrate added. The silver–selenium compound is ignited in a crucible, the residue extracted with nitric acid, and the selenium finally thrown out as a reddish-brown precipitate by dilution with water. It is collected and dried at 100°.

Healthy teeth contain about 0·056% of selenium, and even in the diseased condition about the same figures for the selenium content are obtained. The urine contains 0·0011% of selenium in the male and 0·0009% in the female person. Most vegetables contain traces of selenium, especially spinach. H. W. B.

Micro-Kjeldahl Methods. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1917, **100**, 190—201).—A detailed description of the Kjeldahl method applied to the estimation of nitrogen in small amounts of materials, such as 0·5 c.c. of urine or 10 mg. of an amino-acid. H. W. B.

Estimation of Phosphorus in Cast Iron. ALFREDO CAVAZZI (*Ann. Chim. applicata*, 1917, **8**, 1—6).—The author modifies the

usual process by dissolving the iron in nitric acid and then converting the ferric nitrate, not into oxide and subsequently chloride, but into ferric sulphate, from the solution of which ammonium phosphomolybdate is precipitated in the usual way. In the process described, the ferric sulphate is not heated above 210°, and this is quite safe, as it does not decompose at 350°. R. V. S.

A Simplified Micro-combustion Method for the Estimation of Carbon and Hydrogen. LOUIS ELSBERG WISE (*J. Amer. Chem. Soc.*, 1917, **39**, 2055—2068).—A description of a modification of the Pregl method of micro-analysis of organic substances. The quantity of substance taken is 11—22 mg., and is weighed on an accurate analytical balance of the ordinary type instead of on a micro-balance. For the modifications suggested in the carbon dioxide absorption tube, in the drying train, and in the method of operating, the original should be consulted. D. F. T.

Microchemical Analysis of Explosive Substances. G. KARL ALMSTRÖM (*J. pr. Chem.*, 1917, [ii], **95**, 257—260).—Pregl's method of micro-analysis can be extended to explosive substances if the weighed quantity of the substance under examination is mixed with sand; under such conditions, the combustion can proceed quietly and yield accurate results. Details of the procedure are given, together with the results of analyses of diazobenzenesulphonic acid, silver acetylide, and potassium picrate. In the case of salts of the alkali metals, in order to prevent the formation of a residue of alkali carbonate, it is necessary to mix with lead chromate instead of with sand. D. F. T.

Estimation of Organic Carbon in Water. ATILIO A. BADO (*Anal. Soc. Quim. Argentina*, 1917, **5**, 102—106).—An account of a modification of the Carrasco-Plancher method for estimating organic carbon in sewage and natural waters. It is recommended as both accurate and rapid. A. J. W.

Source of Error in the Analysis of Generator Gas. ALFRED KROPF (*Zeitsch. angew. Chem.*, 1917, **30**, i, 177—179).—The absorption of carbon monoxide by cuprous chloride solution presents certain difficulties and is usually incomplete; the whole of this gas may, however, be absorbed if three absorption vessels are used, the first two containing cuprous chloride solution acidified with hydrochloric acid, and the third ammoniacal cuprous chloride solution. The quantity of nitric oxides formed during the combustion of the residual gases in the explosion pipette may be calculated from the observed contraction, quantity of oxygen used, etc. W. P. S.

Automatic Estimation of Carbon Dioxide (Carbonates) in Soils. Classification of Soils. G. HUTIN (*Ann. Chim. anal.*, 1917, **22**, 158—160).—In the apparatus described the soil is treated with hydrochloric acid in a flask connected with a chamber pro-

vided with a mercury manometer; a float is actuated by the difference in pressure due to the liberation of the carbon dioxide from the soil, and the movements of the float are marked in the usual way on a mechanical recorder. The graph obtained shows whether the carbon dioxide is evolved slowly or quickly from the carbonates in the soils, and thus affords an indication of the kind of carbonate present. W. P. S.

Estimation of Potassium and Sodium in Vegetable Ashes. H. PELLET (*Ann. Chim. anal.*, 1917, **22**, 146—152, 179—185).—The ash is obtained by incinerating the vegetable substance at a relatively low temperature, extracting the carbonised mass with water, igniting the insoluble portion separately, adding this ash to the aqueous solution, and evaporating the latter to dryness; the dry residue is then ignited. In some cases it is necessary to make two extractions with water in order that the carbonised mass may be burnt readily to a white ash. Five grams of the ash are extracted repeatedly with boiling water, the extracts are filtered, and diluted to 500 c.c.; 200 c.c. of this solution are treated with an excess of barium hydroxide solution, the excess of barium hydroxide is converted into carbonate by means of carbon dioxide or ammonium carbonate, and, after filtration, the solution is evaporated with the addition of hydrochloric acid, and the residue of alkali chlorides is ignited and weighed. The potassium in the mixed chlorides is estimated by means of platinum chloride, and the amount of sodium is found by difference. If desired, the potassium platinichloride may be reduced by heating with sodium formate and the reduced platinum collected and weighed. The filtrate and washings from the potassium precipitate may be evaporated to expel ether and alcohol, and the platinum separated by reduction with ammonium formate; the filtrate from the platinum precipitate is evaporated, the residue ignited to expel ammonium salts, then evaporated with the addition of hydrochloric acid, and the residue of sodium chloride weighed. W. P. S.

Estimation of Silver in Organic Compounds. H. J. LUCAS and A. R. KEMP (*J. Amer. Chem. Soc.*, 1917, **39**, 2074—2078).—For the estimation of silver in an organic silver salt, especially of such acids as contain sulphur, it is recommended that a slight excess of *N*/4-sodium cyanide solution be added to 0·3 gram of the substance, and then, after the addition of 10 c.c. of *N*-sodium hydroxide and dilution to 300 c.c., the silver be precipitated as sulphide by the addition of 25 c.c. of *N*/4-sodium sulphide; physicochemical reasons are given for the proportions of the reagents. The advantages claimed include accuracy, speed, and the possibility of recovering the organic acid. D. F. T.

The Blacher Method for the Estimation of Hardness in Water. A. S. BEHRMAN (*Philippine J. Sci.*, 1916, **11**, [*A*], 291—293).—The presence of large quantities of free carbon dioxide renders the estimation of temporary hardness (titration with sodium

carbonate solution) untrustworthy; aspiration for five minutes will reduce the quantity of free carbon dioxide to below 28 parts per million of water, an amount which has no effect on the titration. Sodium chloride, even when present in large amount, does not interfere. In the titration of the total hardness (with potassium palmitate, using phenolphthalein as indicator) the end-point is denoted by the appearance of a light red coloration; the very faint red coloration which first appears should be ignored. This applies particularly to waters containing magnesium salts in addition to calcium salts. W. P. S.

The Estimation of Copper as Sulphide and by Electrolysis. FRIEDRICH L. HAHN (*Zeitsch. anorg. Chem.*, 1917, **99**, 201—248).—It is not possible to obtain pure cuprous sulphide by heating cupric sulphide in hydrogen, as the temperature at which the second atom of sulphur is completely driven off in a reasonable time is very close to that at which reduction to metallic copper takes place. Heating in carbon dioxide in a Rose crucible gives variable results. Many experiments with different kinds of tubes are described, the precipitates being heated in various atmospheres and at known temperatures. If air enters the tube or crucible, oxygen is always absorbed in time, even at moderate temperatures, sulphate being formed with increase of weight. At high temperatures oxygen causes a loss of weight, owing to the formation of cuprous oxide or metallic copper.

Two methods have been found to give satisfactory results. One consists in heating the sulphide in a mixture of hydrogen sulphide and hydrogen, the proportions of which may vary within wide limits. A glazed Rose crucible is used, heating strongly over a Méker burner or blowpipe. During the first part of the heating the gas used is chiefly hydrogen sulphide, and towards the end chiefly hydrogen, separate bubbling tubes being used for the two gases. Two minutes suffice for 0·2 gram of sulphide, ten minutes for larger quantities. The weight becomes quite constant, and the precipitate, being highly crystalline, is not hygroscopic.

Ignition at first in hydrogen sulphide and then in carbon dioxide saturated with methyl alcohol also gives good results.

Copper may be estimated electrolytically in nitric acid solution. When pure platinum electrodes are used, platinum is dissolved at the anode, but platinum–iridium anodes are not attacked. Stationary gauze cathodes or rotating apparatus may be used, and the trace of copper remaining in solution is estimated colorimetrically. C. H. D.

Detection of Mercury for Forensic Purposes. CARLO LUIGI SPICA (*Boll. chim. farm.*, 1917, **56**, 437—440; *Gazzetta*, 1917, **47**, ii, 139—144).—In cases of suspected mercurial poisoning, it is of importance to be able to decide whether the mercury found *post-mortem* was in the form of a soluble or insoluble compound when ingested. From his experiments on viscera preserved in aqueous alcohol, the author finds that mercuric chloride passes in

time into a compound, from which it can be extracted only by the use of hydrochloric acid. When calomel is kept in like manner in contact with visceral material for a long time, it is very doubtful whether any of it is converted into a compound soluble in aqueous alcohol, but a considerable quantity of it is found in a form soluble in hydrochloric acid, and much of it remains apparently unchanged.

R. V. S.

Separation and Detection of Gallium. PHILIP E. BROWNING and LYMAN E. PORTER (*Amer. J. Sci.*, 1917, **44**, 221—224).—Gallium is readily separated, together with glucinum and aluminium, from the other elements by the usual methods; glucinum rarely occurs in products containing gallium, so the latter has only to be separated from aluminium. In a strong hydrochloric acid solution, as little as 0·0002 gram of gallium yields a precipitate with potassium ferrocyanide, but aluminium gives no precipitate. The gallium ferrocyanide may be collected, fused with ammonium nitrate, the iron precipitated with an excess of sodium hydroxide, and the gallium then recovered as hydroxide by heating the filtrate with the addition of ammonium chloride. Traces of zinc may remain in the solution containing the gallium and aluminium and interfere with the ferrocyanide reaction; these traces may be removed by treating the strongly alkaline solution with hydrogen sulphide. Nitrates, or nitric acid, must be removed by evaporation with hydrochloric acid before the ferrocyanide test is applied.

W. P. S.

Analysis of Alloys of Nickel and Zirconium. G. L. KELLEY and F. B. MYERS (*J. Ind. Eng. Chem.*, 1917, **9**, 854).—The following method may be used for the analysis of alloys having the approximate composition: carbon, 0·1 to 0·5%; nickel, 70·0 to 90·0%; iron, 2·0 to 6·0%; silicon, 2·0 to 8·0%; aluminium, 0·5 to 10·0%; zirconium, 2·0 to 18·0%; tungsten, 0·5 to 10%; and manganese, 0·1 to 0·3%. The alloy is dissolved in aqua regia and the solution is evaporated with the addition of sulphuric acid; after dilution, the silica and tungstic oxide are separated by filtration, ignited, and weighed. The silica is then expelled by evaporation with hydrofluoric acid, and the residue of tungstic oxide is weighed. To remove remaining traces of iron, aluminium, and zirconium, this residue is fused with sodium carbonate, the mass treated with water, filtered, the insoluble portion weighed, and the weight deducted from that of the tungstic oxide; the insoluble portion is now fused with potassium hydrogen sulphate, dissolved in water, precipitated with ammonia, and the precipitate then redissolved in hydrochloric acid. The combined solutions from the silica and tungstic oxide are diluted to a definite volume; a portion of this solution is heated, treated with ammonia, the precipitate collected, dissolved in dilute sulphuric acid, and the iron is reduced and then titrated with permanganate solution. To another portion of the solution ammonia is added in excess and the nickel is de-

posited electrolytically. The solution is then boiled to expel most of the ammonia, the precipitated hydroxides are collected, dissolved in hydrochloric acid, and the aluminium is separated by treating the solution with an excess of potassium hydroxide. The ferric and zirconium hydroxides are dissolved, reprecipitated with ammonia, collected, ignited, and weighed; the quantity of iron is found by titration and that of the zirconium by difference. If manganese is present, a further portion of the solution is boiled with the addition of ammonia and ammonium persulphate, the precipitate formed is collected, dissolved in nitric acid with the addition of a small quantity of hydrogen peroxide, the manganese is oxidised with sodium bismuthate, and estimated by one of the usual methods.

W. P. S.

New Volumetric Method for the Estimation of Molybdenum and Vanadium in Steels. TRAVERS (*Compt. rend.*, 1917, **165**, 362—364).—For the estimation of molybdenum the steel is attacked with concentrated hydrochloric acid or by 5% sulphuric acid, potassium permanganate, in just sufficient amount, being used to oxidise the iron, which is then precipitated by pouring the liquid into an excess of boiling aqueous potassium hydroxide. An aliquot portion of the filtrate from this is acidified with hydrochloric acid, so that the liquid contains 1 c.c. of free hydrochloric acid in each 100 c.c. This solution, when cool, is reduced with an excess of titanous chloride, which is titrated back with ferric chloride solution, using potassium thiocyanate as indicator. For concentrations of molybdenum less than 0·05 gram per litre, and under the above conditions, the reduction proceeds according to the equation $2MoO_3 = Mo_2O_5 + O$. Vanadium may be estimated in a similar manner, the reduction being $V_2O_5 = V_2O_4 + O$. If both molybdenum and vanadium are present in the steel, the two are estimated together; the vanadium is then estimated colorimetrically by means of hydrogen peroxide, and the molybdenum obtained by difference. If tungsten is present, it must be eliminated by precipitation prior to the above estimations.

W. G.

Estimation of Tungstic Acid in Wolframite. LUIS GUGLIALMELLI and ULAUS HORDH (*Anal. Soc. Quim. Argentina*, 1917, **5**, 81—90).—The authors point out that there is a liability to error in the ordinary methods of estimating tungsten in wolframite, owing to the formation of complex silicotungstic acids.

A. J. W.

A New Separation of Tin and Tungsten in Stanniferous Wolframs. TRAVERS (*Compt. rend.*, 1917, **165**, 408—410).—The finely powdered mineral is fused with anhydrous sodium sulphide, and the mass, when cold, is broken up with boiling water, diluted to 800 c.c., and feebly acidified. The stannous sulphide is filtered off, along with a little silica and sulphides of iron and manganese, and is purified by solution in ammonium sulphide, con-

taining sulphur. It is reprecipitated by acid and ignited to stannic oxide.

For the estimation of the tungsten, a further portion is fused as above, and the mass dissolved in aqua regia, the solution being evaporated to dryness and the residue taken up with hydrochloric acid. The insoluble residue consists of most of the tungsten in the form of its oxide and some silica. To the filtrate ammonium hydroxide is added in just sufficient amount to precipitate the iron. This precipitate is filtered, washed free from sodium salts, and dissolved on the filter in hot 50% hydrochloric acid. The solution is evaporated to dryness and taken up with hydrochloric acid, the tungsten being left as its oxide. Any silica present in the two tungsten precipitates is separated by the ordinary processes. W. G.

Detection of Germanium and its Separation from Arsenic. PHILIP E. BROWNING and SEWELL E. SCOTT (*Amer. J. Sci.*, 1917, [iv], **44**, 313—315).—The substance, for example, zinc oxide, supposed to contain germanium, is distilled with concentrated hydrochloric acid to which a small quantity of potassium permanganate has been added (compare Buchanan, A., 1916, ii, 486), and the distillate is collected in water contained in a well-cooled receiver. The distillate is then treated with hydrogen sulphide; a white precipitate forms if as little as 0·0001 gram of germanium is present. The potassium permanganate is added to provide the chlorine necessary to prevent reduction of arsenic sulphide and distillation of arsenic; a trace of chlorine may pass into the distillate and produce a cloudiness with hydrogen sulphide, but a precipitate does not form unless germanium is present.

If, as proposed by Winkler (A., 1887, 1081), the mineral is fused with sodium carbonate and sulphur, the mass dissolved in water, the solution treated with ammonium acetate, acidified with acetic acid, and then treated with hydrogen sulphide, any arsenic present is precipitated completely, whilst germanium remains in solution. W. P. S.

Estimation of Tantalum in Alloy Steels. G. L. KELLEY, F. B. MYERS, and C. B. ILLINGWORTH (*J. Ind. Eng. Chem.*, 1917, **9**, 852—854).—The alloy is dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue boiled with hydrochloric acid, and collected on a filter. The filtrate is evaporated to a small volume with the addition of nitric acid, 50 c.c. of concentrated hydrochloric acid are added, the mixture is evaporated to a syrup, and the ferric chloride extracted with ether. The aqueous solution is now heated to expel dissolved ether, evaporated with sulphuric acid, diluted, boiled with the addition of silver nitrate and ammonium persulphate, and then rendered ammoniacal. The precipitate formed contains all of the soluble tantalum and aluminium with traces of chromium, vanadium, and manganese; it is collected, added to the insoluble residue of the first filtration, ignited, and fused with potassium hydrogen sulphate. The mass is treated with hot dilute hydrochloric acid, the insoluble residue of silica

and tantalum oxide is collected, ignited, and the silica is removed by treatment with hydrofluoric acid. If the alloy contains tungsten, it is treated in the first place with a mixture of dilute hydrochloric and nitric acids, the insoluble tungstic oxide is separated, treated with ammonia, and the residue thus obtained is combined with the precipitate obtained at a later stage of the process as described above; the residue of silica and tantalum oxide should, however, be treated with dilute ammonia to remove remaining traces of tungstic oxide. W. P. S.

Modification of the Nicloux Method for Estimating Ethyl Alcohol. E. M. P. WIDMARK (*Skand. Arch. Physiol.*, 1916, **35**, 125—130). **Some Measurements of the Alcohol Content of the Urine in Intoxicated Persons.** E. M. P. WIDMARK (*Hygiea*, 1917, **79**, 158—168; from *Physiol. Abstr.*, 1917, **2**, 342—343).—Five c.c. of urine are boiled for one and a-half minutes with a little kaolin over a free flame, and the distillate is received into a mixture of 5 c.c. of concentrated sulphuric acid and 2 c.c. of 2·3% potassium dichromate, the latter amount being almost reduced by 10 mg. of alcohol. By titration with standard alcohol (0·5% by weight) the tint of the control is matched; the latter is freshly prepared by distilling 10 mg. of alcohol into a similar dichromate mixture. For amounts of alcohol lower than 5 c.c. the amount of dichromate must be halved. Four series of ten determinations with 1·2—7·5 mg. gave results 4·4—0·1% too low. The highest value in urine among twenty-seven cases was 5·7%, much higher than the figures obtained for the blood with Nicloux's method by Schweisheimer. Compare also Pringsheim (A., 1908, ii, 767), who has given a useful method for estimating alcohol in blood. G. B.

Estimation of Glycerol, Crude Glycerol, and Glycerol Lyes. K. LÖFEL (*Zeitsch. angew. Chem.*, 1917, **30**, i, 197—200). —A brief description of the methods which have been described; these include physical methods (distillation, refraction, specific gravity, vapour pressure, etc.), oxidation methods (with permanganate or dichromate), esterification methods (benzoate, acetin, iodide), and various other methods, such as those in which the glycerol is weighed as glyceryl nitrate or sodium glycerate.
W. P. S.

Identification of the Naphthols. A New and Delicate Test for α-Naphthol. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1917, **5**, 97—101).—α-Naphthol gives an intense blue coloration with sodium arsenotungstate, but the β-isomeride gives no coloration with this reagent. A. J. W.

Convenient Filtration Apparatus for the Estimation of Sugar by Titration of the Cuprous Oxide Precipitated from Fehling's Solution. F. BOERICKE (*Zeitsch. angew. Chem.*, 1917, **30**, i, 24).—An Allihn filter tube for the estimation of sugar

is fused into a bulb blown on the end of a short piece of glass tubing which fits, with a ground-glass joint, either into a filter flask or a conical flask. A narrow piece of glass tubing, fitted with a tap, is also fused into the side of the bulb.

The apparatus may be used in either of the following ways. (1) It is fitted into the filter flask, whilst the conical flask is used for the precipitation of the cuprous oxide from Fehling's solution and the sugar. The liquid is then decanted from the cuprous oxide through the filter tube, as also the washings from the cuprous oxide. The rate of filtration in the apparatus can be controlled by manipulation of the tap in the side-tube of the bulb. When decantation and washing are complete, the filter flask is replaced by the conical flask, which contains the main portion of the cuprous oxide. By applying suction to the side-tube, hot ferrous sulphate solution may then be run through the Allihn tube to dissolve the cuprous oxide, and the estimation carried out in the usual way.

(2) The apparatus is fitted into the conical flask, into which filtration takes place directly. The amount of unreduced Fehling's solution in the filtrate is then estimated. T. S. P.

Estimation of Dextrose in Blood. BAUZIL and BOYER (*J. Pharm. Chim.*, 1917, [vii], **16**, 171—179).—The blood is clarified by heating with 25% sodium sulphate solution containing a small quantity of acetic acid and then filtering the mixture. An alternative method consists in shaking the blood with alcohol, filtering the mixture, evaporating the filtrate to expel alcohol, and then treating the liquid with sodium sulphate solution and acetic acid. The dextrose is estimated by Fehling's solution; instead of weighing the cuprous oxide, the excess of copper in the filtrate is titrated with potassium cyanide solution after the addition of ammonia, or the blue solution may be treated with ammonia, a definite volume of standardised potassium cyanide solution, and a small quantity of potassium iodide, and then titrated with $N/10$-silver nitrate solution. W. P. S.

Estimation of the Dextrose in the Blood in Reference to the Condition in which it is Present. HUGH MCGUIGAN and E. L. ROSS (*J. Biol. Chem.*, 1917, **31**, 533—547).—Higher figures for the dextrose in the blood are obtained by the Benedict method than by that of Bertrand when the Fehling's solution employed contains 12·5% of potassium hydroxide. When the strength of the alkali is reduced to 5%, both methods give the same result. It is thought that the difference obtained in the first case is due to the presence of an unknown organic interfering substance which prevents the precipitation of the cuprous oxide. H. W. B.

Estimation of Sugar in Urine. D. SIDERSKY (*Ann. Chim. anal.*, 1917, **22**, 170).—In the volumetric estimation of reducing sugars with Fehling's solution, the addition of magnesium sulphate (5 grams per 500 c.c. of the copper sulphate solution) causes the cuprous oxide to settle rapidly during the titration. W. P. S.

Volumetric Estimation of Sugar in Urine with Fehling's Solution. Ruoss (*Zeitsch. anal. Chem.*, 1917, **56**, 369–384).—The use of the following reagents is recommended: Copper sulphate solution containing 6·9278 grams of copper sulphate and 25 grams of sodium chloride per 100 c.c. Alkaline tartrate solution containing 34·6 grams of potassium sodium tartrate, 10·3 grams of sodium hydroxide, 3 grams of potassium thiocyanate, and 5 grams of sodium chloride per 100 c.c. The end-point of the titration is ascertained by adding 5 c.c. of dilute acetic acid containing 10% of sodium chloride to the hot mixture, followed by 3 drops of 5% potassium ferrocyanide solution; a brown coloration indicates the presence of cupric salts, and the titration must, in this case, be repeated, using a larger volume of the sugar solution. Attention is directed to the fact that urine free from sugar reduces Fehling's solution to an extent which may in some cases be equivalent to the presence of 0·2% of reducing sugar. W. P. S.

The Possibilities and Limitations of the Duclaux Method for the Estimation of Volatile Acids. L. J. Gillespie and E. H. Walters (*J. Amer. Chem. Soc.*, 1917, **39**, 2027—2055).—A review and examination of the method of Duclaux (this Journ., 1875, 188) for the investigation of a mixture of volatile fatty acids in aqueous solution by the behaviour on distillation. Algebraic and graphic methods for the computation of the results for mixtures of two or three acids are described, and the algebraic calculation for four or more acids is indicated. Application of the method to known mixtures shows that with two or three acids present, a quantitative analysis may be made without very great error; if the method is to be applied to mixtures of more than three acids, the mixture must first be resolved by fractionation into portions containing only three acids. D. F. T.

Estimation of Salicylic Acid in Foods. H. D. Steenbergen (*Chem. Weekblad*, 1917, **14**, 914—921).—An investigation of various methods of estimating salicylic acid in foods. A. J. W.

A very Delicate Reaction of the Nitriles. S. Dezani (*Atti R. Accad. Sci. Torino*, 1917, **52**, 826—833).—When a solution of a nitrile (aliphatic or aromatic) is treated with an equal volume of hydrogen peroxide (12 vols. %) and 2—3 drops of a 5% solution of ferric chloride, hydrogen cyanide is produced on boiling. This can be detected by test papers made by treating filter-paper with picric acid (1%), drying, and then immersing the paper in a 10% solution of sodium carbonate. If much nitrile is present, the paper turns blue, but with smaller quantities a red or brownish-red coloration is observed. Very small quantities of nitrile can be detected in this way, the limit being about 2×10^{-5} gram of HCN. The reaction is applied to the detection of nitriles in urine. R. V. S.

Cryoscopy and Refractometry of Milk. J. Pritzker (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 69—112).—It is now established that the

freezing point of milk varies but very little from -0.55°, and that it is not affected by the breed, age, feeding, or time of milking of the cows. It is influenced, however, by the acidity of the milk and by the presence of preservatives; each degree of acidity (Soxhlet-Henkel scale) decreases the freezing point by about 0.008°, and the addition of 0·1% of formaldehyde decreases it by 0.03°. Potassium dichromate raises the freezing point. The use of calcium chloride in the preparation of milk serum has an influence on the freezing point and refractometer number of the serum according to the quantity of calcium chloride added; the freezing point of the serum is lower than the sum of the freezing points of the milk and the added quantity of calcium chloride solution. The freezing point of milk varies correspondingly with the refractometer number.

W. P. S.

Application of the Cryoscopic Method for Estimating Added Water in Milk. J. T. KEISTER (*J. Ind. Eng. Chem.*, 1917, **9**, 862—865).—The freezing point of milk (-0.54° to -0.57°) affords the most trustworthy basis on which to draw conclusions as to the presence or absence of added water in milk. In the greater number of cases the presence of as little as 5% of added water can be detected by the method. It is essential that the process be applied only to fresh milk, since the freezing point is lowered by about 0.003° for each 0·01% increase of acidity. The presence of formaldehyde lowers the freezing point. The method may be used in milk-control work, as it need be applied only to samples of doubtful character.

W. P. S.

Braun's Reagent. I. J. RINKES (*Chem. Weekblad*, 1917, **14**, 895—896. Compare Braun, A., 1908, i, 700).—An account of the application of Braun's reagent to the detection of aldehydes, and to the distinguishing of ketoaldehydes and dialdehydes.

A. J. W.

Estimation of the Acetone Substances in Urine, together with an Altered Procedure for a Separate Estimation of Acetone and Acetoacetic Acid in Urine. N. O. ENGFELDT (*Zeitsch. physiol. Chem.*, 1917, **100**, 93—110).—The author, finding that the method for the separate estimation of acetone and acetoacetic acid in urine described by Lenk (this vol., ii, 399) is not satisfactory, proposes the following modification, which furnishes nearly accurate results. One hundred c.c. of 5% potassium permanganate are diluted with 100 c.c. of water and acidified with 1 c.c. of acetic acid. To this, 10 c.c. of urine are added, and the mixture distilled for twenty minutes into 100 c.c. of water. The distillate is diluted to about 300 c.c., 20 c.c. of 25% sodium hydroxide and 10 c.c. of 3% hydrogen peroxide are added, and the mixture again distilled for thirty-five to fifty minutes. The acetone in the second distillate is estimated by the Messinger method, and constitutes the acetone preformed in the urine. The total acetone plus aceto-acetic acid is estimated in the usual way by the Messinger method, and the difference between the two results represents the aceto-

acetic acid, calculated as acetone, in the original urine. The result obtained is stated to be about 5% less than that actually present.

From 80% to 90% of the total acetone in a fresh urine is usually present in the form of acetoacetic acid. H. W. B.

Estimation of Ferricyanides by Titration with Permanganate. C. DE COQUET (*Bull. Soc. Pharm. Bordeaux*, 1917; from *Ann. Chim. anal.*, 1917, **22**, 160—161).—The solution, containing about 0·25 gram of ferricyanide, is gently heated with the addition of 0·5 gram of aluminium and 25 drops of sodium hydroxide solution; the reduction of the ferricyanide requires about twenty minutes. The mixture is then diluted, filtered, the filtrate acidified with sulphuric acid, and titrated with $N/10$-potassium permanganate solution; each c.c. of the latter solution is equivalent to 0·033 gram of potassium ferricyanide. When the quantity of ferricyanide present is less than 0·5 gram, 0·2 c.c. is deducted from the volume of permanganate solution used. The method may be employed for the estimation of ferricyanide in certain photographic powders, which also contain uranium nitrate, ammonium iron citrate, and copper chloride. The powder is dissolved in water, the solution rendered alkaline with sodium hydroxide, diluted to 50 c.c., filtered, and 25 c.c. of the filtrate are taken for the estimation as described. W. P. S.

Effect of Temperature on the Reaction of Lysine with Nitrous Acid. BARNETT SURE and E. B. HART (*J. Biol. Chem.*, 1917, **31**, 527—532).—By raising the temperature, the reaction between lysine and nitrous acid is accelerated, and, above 30°, all the nitrogen is expelled in ten minutes. It is sufficient, therefore, if the temperature is raised to 30° or over, to shake the hexone bases in the Van Slyke method of protein analysis for fifteen minutes instead of for thirty minutes, as usually recommended. At temperatures of 1° and under, the ϵ-amino-group of lysine does not react with nitrous acid. H. W. B.

Identification of the Poisons Extractable from Acid Aqueous Solution by Means of Ether according to the Stas-Otto Process (Veronal, Acetanilide, Salicylic Acid, Phenacetin). O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 289—292, 298—299; from *Chem. Zentr.*, 1917, ii, 137—139).—The microchemical identification of the above-mentioned substances is effected as follows. *Veronal.*—Zinc chloroiodide solution is added to the sublimate from the veronal residue beneath a cover slip; numerous, generally small (up to 40 μ long and 20 μ wide), flat, tabular, and prismatic crystals are immediately formed, which vary in colour from pale grey to blackish-red. They are optically biaxial, have extraction parallel to the long axis, are rhombic, and show strong pleochroism (colourless to blackish-red). The crystals are stable. Acetanilide and salicylic acid do not react with zinc chloroiodide. The veronal sublimate is dissolved by hydriodic acid, and crystals

are slowly deposited at the edges of the solution; these are relatively large (up to 150 μ long and 50 μ wide), flat, red, or sometimes grey, optically biaxial, have direct extinction, and shine red between crossed Nicols. With bromine-potassium bromide solution, a red colour is developed, due to a mixture of flesh-coloured and red needles and leaflets, which polarise strongly and show direct extinction and very marked pleochroism. They attain a length of 50—80 μ, whilst, also, very small groups of yellow crystals are formed. The red crystals disappear in course of time, whilst the yellow are more stable. If the veronal sublimate is dissolved in ammoniacal copper solution and the latter allowed to evaporate, a mixture of pink to violet lamellæ and coarse plates is obtained, which shines in polarised light. The plates belong to the monoclinic system, are optically biaxial, and have oblique extinction.

Acetanilide.—Well-formed crystals are obtained by sublimation and recrystallisation from water. With hydriodic acid, reddish-brown drops are formed immediately, from which crystals of iodoacetanilide separate after a few minutes. These are strongly dichroic (reddish-brown and pale yellow), and show extinction parallel to the long axis. They are stable. Bromoacetanilide is prepared by the addition of bromine-potassium bromide solution to the sublimate dissolved in hot water; a yellow solution results, from which, on addition of water, colourless crystals separate. These consist of fine needles, which are transformed partly into prismatic aggregates and partly into small, monoclinic crystals. The *iso*nitrile test, the identification of aniline after hydrolysis, and certain colour reactions can also be performed.

Salicylic Acid.—Sublimation can be effected without decomposition of the acid into carbon dioxide and phenol. Better crystals are obtained after solution of the sublimate in water. They consist of prismatic rodlets and coarse, generally rectangular prisms, which belong to the monoclinic system, polarise in all colours, and have oblique extinction. The sublimate was tested with iron chloride, nitric acid, and Millon's reagent, and also converted into the methyl ester (recognised by odour). If the sublimate is treated with ammonia, the solution allowed to evaporate, and silver nitrate added to the moist residue, a mixture of crystals is formed containing well-developed, oblique prisms of silver salicylate. The latter are up to 100 μ long and 15 μ wide; they polarise strongly, and have oblique extinction (monoclinic).

Phenacetin.—The sublimate should be recrystallised from water, from which the phenacetin separates in two forms. The first of these consists mainly of flat prisms with oblique ends, at which twin-formation is frequently evident; they are 15—20 μ wide and 100—150 μ long. The subsidiary form comprises very long, flat, rectangular prisms, which invariably exhibit strong, oblique grooves. The oblique and rectangular prisms have oblique and direct extinction respectively. All the crystals polarise strongly. Platelets, as with acetanilide, are not formed. Characteristic nitrophenacetin crystals are prepared by mixing the sublimate with water and nitric acid and warming without cover-glass until a yellow rim is formed.

Groups of yellow needles soon separate, which polarise strongly between crossed Nicols; slender needles, prisms, or long, flat, rectangular crystals with direct extinction are also produced. When similarly treated, salicylic acid, acetanilide, or antipyrine yield only a colourless rim and white crystals. The phenacetin sublimate does not give the carbylamine reaction. The tests with hydriodic acid and bromine–potassium bromide solution are also described.

H. W.

Improved Test for Indican in Urine. F. C. ASKENSTEDT (*J. Lab. and Clin. Med.*, 1917, **2**, 578—580; from *Physiol. Abstr.*, 1917, **2**, 345).—The urine is diluted to D 1·005, warmed, and shaken with chloroform; Obermayer's reagent is then added, and the indigo shaken into the chloroform. If the latter remains colourless or only shows a trace of blue, the urine is normal; otherwise there is excess of indican. G. B.

A Source of Error in the Investigation of Urinary Indoxyl. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 93—94).—In the examination of urine for indoxyl, contradictory results are sometimes obtained by different methods. The author attributes this phenomenon to the presence of the "scatolic colours" of Porcher and Hervieux. A. J. W.

Reaction of Antipyrine with *p*-Dimethylaminobenzaldehyde. CLAUDE GAUTIER (*Soc. Biol.*, 1917; from *J. Pharm. Chim.*, 1917, [vii], **16**, 189).—An orange coloration is obtained when a mixture of 10 c.c. of an aqueous antipyrine solution (containing 0·1 gram of the substance) and 1 c.c. of an alcoholic 5% *p*-dimethylaminobenzaldehyde solution is acidified with 1 c.c. of concentrated hydrochloric acid. W. P. S.

The Sensitiveness of the General Method of Extraction of Alkaloids in Water. L. LAUNOY (*Compt. rend.*, 1917, **165**, 360—362).—The method employed, namely, to make the water alkaline with sodium carbonate and subsequently to extract it three times with chloroform, is capable of detecting 1 part of alkaloid in two million parts of water. Two hundred c.c. of water should be extracted, the residue from the chloroform extract after evaporating off the chloroform being dissolved in 1 c.c. of 10% sulphuric acid. The acid solution is divided into two parts, one being tested with Tanret's reagent and the other with Bouchardat's reagent. W. G.

Titration and Estimation of Morphine with Iodic Acid. JITENDRA NATH RAKSHIT (*J. Soc. Chem. Ind.*, 1917, **36**, 989—990).—The process depends on the fact that when a solution of morphine is treated with an excess of iodic acid in the presence of dilute sulphuric acid, the oxidation of the alkaloid is quantitative, two molecules of morphine absorbing three atoms of oxygen. In the estimation, morphine, either in the form of the free base, hydro-

chloride or sulphate (0·05—0·15 gram), is thoroughly shaken with water (50 c.c.), *N*/10-sulphuric acid (5 c.c.), and freshly prepared cooled starch solution (1%, 10 c.c.); *N*/5-iodic acid solution (5—15 c.c.) is introduced, the mixture again shaken, set aside in a dark place for about fifteen minutes, and titrated back with *N*/10-thiosulphate solution. The end-point should be taken when the blue colour has remained discharged for at least thirty seconds.

The method cannot be applied to the estimation of morphine in opium, the results obtained being too high and discordant, owing to the fact that codeine and narcotine also absorb a certain amount of oxygen under the same conditions. In addition, other substances are present in opium which likewise absorb oxygen. H. W.

Colorimetric Methods for the Estimation of very small Quantities of Morphine. A. HEIDUSCHKA and MARTIN FAUL (*Arch. Pharm.*, 1917, **255**, 172—191).—I. *Georges and Gascard's Iodic Acid Method* (A., 1906, ii, 507).—The authors employ a modification of this method. Instead of using a Duboscq colorimeter, they prepare a scale of colours by diluting a faintly acid solution of morphine in about *N*/10-hydrochloric acid to a concentration of 1 in 1000 and then preparing from this a series of solutions of concentrations down to 1 in 10,000. Equal volumes (10 c.c.) of these solutions are treated with 5 c.c. of 5% iodic acid solution, and the yellow colorations are examined after about half a minute. The differences in colour are more pronounced in the more dilute solutions. Whilst morphine can be thus detected at a concentration of 1 in 12,500, quantitative observations can only be made at concentrations between 1 in 1500 and 1 in 5500.

The method is rendered more sensitive if 1 c.c. of 10% aqueous ammonia is added about five minutes after the addition of the iodic acid. Morphine can thus be detected at a concentration of 1 in 18,500 and estimated at concentrations between 1 in 5000 and 1 in 16,500.

II. *Estimation with Marquis's Reagent.*—One c.c. of the morphine solutions prepared as above is evaporated in a small basin, the residue is treated with 1 c.c. of Marquis's reagent (2—3 drops of 40% formaldehyde solution, 3 c.c. of conc. sulphuric acid), and the violet solution is washed into the comparison tube with 4 c.c. of sulphuric acid. The colours are examined by transmitted light, since in reflected light an actual colour change from blue to bluish-brown renders the comparison untrustworthy. Morphine can thus be estimated at concentrations between 1 in 1400 and 1 in 14,000, and, the dilution with the sulphuric acid being omitted, can be detected at a concentration of 1 in 25,000.

Two samples of ripe poppy capsules examined by these methods were found to contain 0·017 and 0·068% of morphine respectively; in both cases the seeds did not contain morphine. C. S.

Detection and Presence of Carotinoids in Plants. C. VAN WISSELINGH (*Flora*, 1917, **177**, 371—432; from *Physiol. Abstr.*, 1917, **2**, 365).—The best method for obtaining crystals is by

Molisch's potassium hydroxide method; the following reagents may be used: saturated solutions of antimony trichloride and of zinc chloride in 25% hydrochloric acid, or saturated solution of anhydrous aluminium chloride in 38% hydrochloric acid. The author assumes the existence of various carotinoids; in many cases two are found in the same preparation. G. B.

Simple New Reaction for Bile Pigments. Josef Kallós (*Deut. med. Woch.*, 1917, **46**, 751; from *Chem. Zentr.*, 1917, ii, 136).—The urine (5—8 c.c.) is shaken with dilute hydrochloric acid (1—2 c.c.) and 2—3 drops of potassium or sodium nitrite (0·5%) are added; a pale to olive-green coloration is developed according to the quantity of bile pigment present. H. W.

Use of Alkalis in Quantitative Analytical Investigations. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1917, **5**, 95—96).—In estimating egg-albumin, asparagine, peptone, and urea by Schloesing's method, the author observed that the results are materially influenced by employing different alkalis. A. J. W.

Rapid Volumetric and Clinical Estimation of Albumin. Ed. Justin-Mueller (*Bull. Sci. Pharmacol.*, 1917, **24**, 29—32; from *Chem. Zentr.*, 1917, i, 977).—The process depends on the union of potassium ferrocyanide with albumin. A mixture of clear, filtered urine (10 c.c.), water (80 c.c.), and acetic acid (5%, 10 c.c.) is titrated with potassium ferrocyanide solution (0·126%). A solution of iron alum (10 grams), acetic acid (10 c.c.), and water (80 c.c.) is used as indicator. If the urine contains 0·5—2 grams of albumin, it is diluted 1 in 10; with higher albumin content, it is diluted 1 in 100. The titration is finished when a drop of the liquid gives an immediate sky-blue coloration with a drop of the indicator. If the urine is insufficiently dilute, the first 3·5 c.c. of the reagent cause a finely divided, voluminous precipitate which obscures the end-point. In this case, either the urine is diluted with ten times its volume of water and the estimation is repeated, or the end-point is determined by means of copper sulphate solution (10%). [Three to four drops of liquid are mixed with one drop of copper sulphate solution. The end-point is indicated by the appearance of a faint reddish-brown coloration.] 0·1 C.c. of the above potassium ferrocyanide solution corresponds, with undiluted urine, with 0·01 gram of albumin per litre. The initial 3·5 c.c. of the reagent are necessary for the saturation of the acidified water, and must therefore be deducted. The urine is free from albumin if the iron–alum reaction occurs immediately after addition of 3·5 c.c. of the reagent. H. W.

Rapid Method for the Estimation of Albumin and Sugar in Urine. Emil Lenk (*Zeitsch. angew. Chem.*, 1917, **30**, ii, 45—48. Compare A., 1916, ii, 163; this vol., ii, 341).—In the estimation of albumin in urine by Esbach's method (precipitation with picric and citric acids), the addition of a very small quantity of

finely powdered pumice-stone causes the precipitate to settle completely within ten minutes. When reducing sugars are estimated volumetrically with Fehling's solution, the addition of magnesium sulphate to the copper sulphate solution decreases the time required for the separation of the precipitated cuprous oxide; 10 grams of magnesium sulphate per litre of the copper sulphate solution are sufficient. W. P. S.

A New Process for the Estimation of Reducing Substances in Urine. CHARLES RICHET and HENRY CARDOT (*Compt. rend.*, 1917, **165**, 258—262).—The reagent used is $N/50$-potassium permanganate, made up in $3N/100$-sulphuric acid, and the method is a measure of the reducing substances other than carbamide in the urine. It gives what the authors call the "manganic index" of the urine, that is, the number of litres of the $N/50$-permanganate decolorised in twenty-four hours at the ordinary temperature by the total urine excreted in twenty-four hours. Into each of twelve test-tubes are placed 10 c.c. of the permanganate solution. The urine is diluted to ten times its volume with water, and into the permanganate, in successive tubes, are run 0·5, 0·6, . . . 1·6 c.c. of the diluted urine At the end of twenty-four hours, these tubes are examined for two consecutive tubes, one of which will be decolorised and the other tinged pink. Knowing the amounts of diluted urine run into these tubes, the "manganic index" can be calculated. This will vary in the healthy individual from 50 to 250, but is moderately stable with the same individual on a uniform diet. It bears no relationship to the carbamide excretion or to the total quantity of organic substances other than carbamide present in the urine. W. G.

Culture Media employed in the Bacteriological Examination of Water. IV. Neutral-red Lactose Peptone Media. E. M. CHAMOT and C. M. SHERWOOD (*J. Amer. Chem. Soc.*, 1917, **39**, 1755—1766).—A solution containing 3—4% of peptone, 0·8% of potassium chloride or sulphate, 0·6% of lactose, and 0·008% neutral-red, with an acidity of $+1\pm0{\cdot}2\%$, furnishes a sensitive medium for the rapid detection of fæcal pollution by bacteria; the addition of meat-broth increases the sensitiveness, but is not essential. The yellow, fluorescent compound formed by the action of the bacteria is probably dimethyldiaminomethylhydrophenazine, a simple reduction product of neutral-red, into the composition of which ammonia does not enter. The Stokes neutral-red medium is a convenient and trustworthy one for the detection of fæcal contamination in water, and is more sensitive than lactose-bile.

T. H. P.

General and Physical Chemistry.

A New Proof of the Existence of Molecules. VI. The Absorption of Light by Molecular and Colloidal Solutions of Sulphur. NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1917, **92**, 471—495).—In continuation of previous observations on the absorption of light by colloidal solutions of variable dispersity (compare A., 1913, ii, 2), quantitative measurements have been made of the absorption of ultra-violet light ($\lambda = 250$—$700\ \mu\mu$) by molecular and colloidal solutions of sulphur. The degree of dispersity of the colloidal solutions prepared by different methods varies within wide limits, the most highly disperse solutions being those prepared according to the methods of Wackenroder and Raffo. These solutions were fractionated by Odén's method, and the spectrophotometric observations were thus made on solutions containing particles of approximately the same size.

The results obtained show clearly that the character of the absorption curves changes continuously with decrease in the size of the colloidal particles, and that the absorption of a molecular solution of sulphur in ethyl alcohol corresponds with that of a limiting colloidal solution. The colloidal solutions containing particles for which the average diameter is $550\ \mu\mu$, give a flat absorption curve without any evidence of a maximum. For particles of average diameter $= 160\ \mu\mu$, the absorption is greater, and a maximum is found at $\lambda = 340\ \mu\mu$. In the case of particles of diameter $= 110\ \mu\mu$, the maximum shifts to $\lambda = 280\ \mu\mu$. For more highly dispersive solutions, no maximum was found within the limits of observation, but with diminishing size of the particles the curve of absorption approximates continuously to that of the molecular solution.

Incidentally, it was shown that the absorption of the colloidal solutions is in satisfactory agreement with Beer's law.

H. M. D.

The Light Absorption of an Aqueous Solution of Sodium Sulphate. E. O. HULBERT and J. F. HUTCHINSON (*J. Physical Chem.*, 1917, **21**, 534—535).—Measurements of the absorption of light by a solution of sodium sulphate at temperatures between 20° and 40° show that the absorption undergoes no change at the temperature at which Glauber's salt is transformed into the anhydrous salt.

H. M. D.

Colour and Chemical Constitution. II. Spectra of the Mixed Phthaleins and of the Sulphone-phthaleins. JAMES MOIR (*Roy. Soc. South Africa*. Compare this vol., ii, 349).—Mixed phthaleins containing two different phenol residues, one of which is $C_6H_4 \cdot OH$, are readily obtained by boiling *p*-hydroxybenzophenone-*o*-carboxylic acid with phenols or amines, whether free or

substituted. The spectra of eighteen new phthaleins of this class are described and the relations between them discussed. The spectrum of the mixed phthalein affords a convenient method for the identification of phenols, amines, their ethers, and other derivatives.

The spectra of five sulphone-phthaleins and of six further new derivatives of phenolphthalein have also been examined.

H. M. D.

Absorption Spectra of some Polyhydroxyanthraquinone Dyes in Concentrated Sulphuric Acid Solution and in the State of Vapour. DAVID B. MEEK (T., 1917, **111**, 969—988. Compare A., 1916, ii, 364).—The new observations on the absorption of polyhydroxyanthraquinone dyes in the state of vapour and in sulphuric acid solution are compared with the results previously obtained for alcoholic and potassium hydroxide solutions. The nature of the solvent influence is such that the absorption maximum is displaced towards the red end of the spectrum by solution in sulphuric acid and in aqueous potassium hydroxide when comparison is made with alcoholic solutions. Excepting the case of purpurin, the displacement is greater for the potassium hydroxide solutions. The resolution is more pronounced in sulphuric acid solution, and this solvent increases the relative intensity of the absorption towards the violet end of the spectrum.

According to observations on alizarincyanin in various organic solvents, the position of the maximum absorption varies for the most part in agreement with Kundt's rule, but this rule does not apply to acid and basic solvents.

The changes produced by variation in the number and position of the auxochromes show that the approximation of the auxochromes in the benzene nucleus is accompanied by a displacement of the bands towards the red end of the spectrum and by a decrease in the intensity of the bands relative to their breadth. H. M. D.

The Distribution of the Active Deposit of Radium in an Electric Field. S. RATNER (*Phil. Mag.*, 1917, [vi], **34**, 429).—The paper establishes conclusively by a large number of experiments the importance of the electric wind, produced by an electric field in an ionised gas, on the distribution of the active deposit of radium, and has reference especially to the explanation of the origin of the anode activity which is always obtained in greater amount the greater the quantity of emanation employed. When a plate covered with radium-*A* is charged, the electric wind is directed from the active surface and carries away the recoil atoms of radium-*B*. Those atoms that lose their initial charge by recombination with ions may be carried by the wind through long tubes, and even caused to circulate continuously through a system of tubes without showing any tendency to deposit on the walls. In this way, a slow current of discharged recoil-atoms of radium-*B* was caused to circulate through a vessel provided with an insulated

electrode, and their distribution in an electric field investigated. Since they are not charged, they should not be affected by an electric field, but it was found they could be collected on a charged plate independently of the sign of the charge. That this is due to the electric wind in the ionised gas, which in this case of uniform ionisation in the gas is partly directed to the plate and partly to the sides of the vessel, was shown by introducing an additional strong source of ionisation into the chamber, so arranged that the electric wind it created was directed towards or away from the charged plate, which in the first case acquired a largely increased activity and in the second acquired practically none. It was shown that the circulation of uncharged radium-*B* recoil-atoms may continue after all the radium-*A* that gave rise to them has disappeared, and charging the electrode for a few minutes after this has occurred causes the plate to become nearly as active as if kept charged throughout the whole period.

Experiments showed that the anode activity obtained when a field is established in a vessel containing radium emanation is due to uncharged particles of the active deposit carried to the anode by the electric wind. If a strong additional source of ionisation was arranged to direct the electric wind from the cathode on the anode, the activity deposited on the anode could be increased to twenty times as great as the cathode activity. In a vessel where large quantities of emanation have been stored, which is therefore coated internally with polonium, the activity collected on the anode is always the same as that collected on the cathode. Using a needle electrode charged to a high potential (15,000 volts), positive or negative, the electric wind from it prevents it receiving any appreciable amount of active deposit. In an uncharged vessel containing emanation, the amount of active deposit on a plate may be largely increased by directing a blast of air against it. The motion of the so-called large radioactive ions in an electric field is to be explained by electric wind effects, not by their carrying a charge. The rate of recombination of radioactive ions is shown to be greater than that of ordinary gaseous ions. F. S.

The Theory of Decay in Radioactive Luminous Compounds. J. W. T. Walsh (*Proc. Roy. Soc.*, 1917, **93** *A*, 550—564).—Rutherford's theory of the destruction of active "centres" in a luminous compound by the passage of the α-ray leads to a simple exponential decay curve, whereas the luminosity of radium luminous compounds decreases exponentially for about 200 days from manufacture, and then the rate of decay decreases, tending to approach a limiting value that is not zero (Paterson, Walsh, and Higgins, *Proc. Phys. Soc.*, 1917, **4**, 215). The theory advanced to explain the discrepancy is that the destroyed active centres recover at a rate proportional to their concentration in the material. This leads to the expression $\log(B_t - m) = Kt$, where B_t is the brightness at time t and m and K are constants, which agrees closely with the observations on eight different samples. For the value of the

constants, the full paper must be consulted. In two applications of the theory, (1) the total light emitted by the compound during varying intervals from the time of manufacture, and (2) the variation of the final luminosity of a compound with its content of radium, are calculated. The latter leads to the conclusion that there is no advantage commensurate with cost in using a compound with a greater radium content than 0·2 or at most 0·3 mg. of radium per gram of zinc sulphide. In an appendix, the application to mesothorium compounds is given, and curves are given for the theoretical luminosity against time in years (up to two years) for specimens of mesothorium, respectively, six months, one year, and two years old. F. S.

Radioactivity of Philippine Waters. J. R. WRIGHT and GEORGE W. HEISE (*J. Physical Chem.*, 1917, **21**, 525—533).—Some ninety different waters, chiefly from springs and flowing wells, have been examined for radioactivity. The waters as a whole show no abnormal features. The highest emanation content met with in a deep-well water was equivalent to 21×10^{-10} grams of radium per litre, and the highest in a spring water to 13×10^{-10} grams. There is no apparent general relation between the chemical quality of a water and its radioactivity.

Tests for the actual radium content of some twenty typical waters showed that the observed radioactivity was due to emanation absorbed from materials with which the ground water had been in contact, and was not due to dissolved radium salts. H. M. D.

Redetermination of the Heat of Vaporisation of Water. J. HOWARD MATHEWS (*J. Physical Chem.*, 1917, **21**, 536—569).—The apparatus used is, in principle, the same as that described in a previous paper (Richards and Mathews, A., 1911, ii, 697), but various improvements have been made in detail, including the substitution of a vaporiser made of transparent quartz for the glass vessel previously used, and the employment of a superior type of adiabatic calorimeter.

In preliminary experiments, the possible error due to priming of the water vapour was examined, but it was found that the improved form of apparatus is free from errors arising from this cause. The results obtained in the actual measurements of the heat of vaporisation show clearly the dependence of the values on the rate of condensation, thus confirming the earlier experiments. The relation between the observed heat of vaporisation and the rate of condensation is approximately linear, and by extrapolation the influence of this factor can be eliminated. The value thus obtained for the heat of vaporisation of water at 100° is 539·0 cals. when expressed in terms of the 15° cal. H. M. D.

Heats of Dilution. I. A Calorimeter for Measuring Heats of Dilution. II. The Heat of Dilution of 3*N*-Ethyl Alcohol. D. A. MACINNES and J. M. BRAHAM (*J. Amer. Chem. Soc.*, 1917, **39**, 2110—2126).—The calorimeter described is a modified

form of the adiabatic calorimeter devised by Richards (A., 1910, ii, 391, 930), which not only eliminates the heat change due to radiation and conduction, but also the heat effect due to stirring. This result is achieved by making the temperature of the environment slightly lower than that of the calorimeter itself, the difference of temperature required being found by trial. When this temperature difference is correctly adjusted, a thermometer inserted in the calorimeter remains constant for an indefinite length of time.

The calorimeter has been used to measure the heat of dilution of 3*N*-ethyl alcohol with varying amounts of water. From the data thus obtained, the authors have calculated the reversible heat of dilution, defined as the heat change which occurs on the addition of 1 mol. of solvent to an infinite quantity of solution. The value of this reversible heat of dilution is 21·80 cal. H. M. D.

Surface Tensions of the Co-existing Layers of Systems of Mutually Soluble Liquids. J. Livingston R. Morgan and Ward V. Evans (*J. Amer. Chem. Soc.*, 1917, **39**, 2151—2171).—The surface tensions of the conjugate solutions formed by water in combination with phenol, amyl alcohol, and triethylamine have been measured at various temperatures by the drop-weight method.

For water and phenol it is found that the curves obtained by plotting the surface tensions of the conjugate solutions against the temperature intersect at 45°, and that the curve for pure phenol passes through the same point. Below 45° the aqueous layer has a lower surface tension than the phenol layer, but at somewhat higher temperatures the order is reversed. The two curves begin to approach each other, however, at some temperature in the neighbourhood of 60°, and become identical at the critical solution temperature, 68·8°.

The surface tension-temperature curves for conjugate solutions of amyl alcohol and water between 0° and 55° diverge with increase in the temperature. The surface tension of both the solutions is much nearer to the value for the alcohol than to that for water.

The curves for triethylamine and water between 25° and 45° point to convergence at about 19°, but accurate measurements could not be made in the neighbourhood of the critical solution temperature by reason of the rapid change in the concentration of the conjugate solutions. It is pointed out as worthy of attention that the aqueous layer increases in surface tension with increase in temperature.

Some observations on the effect produced by the addition of small quantities of water to pure phenol show that this increases the surface tension, the increase attaining a maximum value for a quantity of water which becomes smaller as the temperature falls.

The surface tension of amyl alcohol between 0° and 50° is given by $\gamma = 24{\cdot}450 - 0{\cdot}07308t$, and that of triethylamine between 0° and 40° by $\gamma = 21{\cdot}987 - 0{\cdot}09970t$. H. M. D.

Device for Accelerating Dialysis. H. Thoms (*Ber.*, 1917, **50**, 1235—1240).—The apparatus consists of two chambers (for example, the covers of vacuum desiccators) clamped together with a sheet of

parchment between them, and arranged on a framework, so that it can be mechanically rotated about the plane of the membrane. One chamber contains water and the other the liquid to be dialysed, both being only half full. As the apparatus revolves, the liquids glide over the membrane and the separation of the crystalloid is two or three times as efficient as in stationary dialysers, especially in the case of dilute solutions.

The process is termed "gliding dialysis," and is specially designed for the preparation of stable fruit syrups which contain the fragrant constituents and enzymes of the fruit juice in the undecomposed state. J. C. W.

Diffusion and Osmosis under the Influence of Electrocapillary Forces. TONI HAMBURGER (*Zeitsch. physikal. Chem.*, 1917, **92**, 385—420).—According to Girard (compare A., 1914, ii, 718), the phenomena of diffusion and osmosis are largely influenced by the electrical charge of the membrane concerned. The experiments described consist for the most part of observations similar to those previously made by Girard, but the results obtained differ appreciably in some respects and lead to the conclusion that electrocapillary forces do not play any essential part in connexion with the phenomena of diffusion, although the osmosis is influenced by the electrical charge of the membrane. The variation in the magnitude and sign of the charge is probably to be explained in terms of adsorption and hydration of the ions. H. M. D.

Dissociation of Complex Double Salts in Aqueous Solutions. HAROLD L. MAXWELL (*Chem. News*, 1917, **116**, 247—250).—The changes which occur when solutions of double salts are allowed to diffuse into water have been examined in a series of experiments with sodium cadmium bromide, ammonium zinc bromide, ammonium copper chloride, and ferrous ammonium sulphate. The results show that diffusion leads to a partial separation of the component simple salts. H. M. D.

Vapour-pressure Isotherms of Substances with Gel Structure. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1917, **100**, 1—76).—The ultra-microscopic structure of gelatin and silica gels has been demonstrated (A., 1912, ii, 145), but concentrated gels are found to be amicroscopic, and other methods must be used to determine their structure. Zsigmondy has shown (A., 1911, ii, 880) that the dimensions of the structure may be calculated from the vapour pressure isotherms, the vapour pressure of liquid enclosed in very fine canals being lower than that of the same liquid with a free surface. The theory is only applicable to gels in which the liquid is chemically indifferent towards the enclosing substance. In addition to gelatin, a natural silica gel (hydrophane from Hubertusburg), permutite, and coconut charcoal have now been investigated by this method. A vacuum apparatus is used (A., 1912, ii, 641), and the vapour pressure is regulated by using mixtures of alcohol and glycerol, benzene and paraffin, or sulphuric acid. In all cases the

ascending and descending vapour pressure isotherms form a characteristic hysteresis diagram, similar to those obtained by van Bemmelen for colloidal hydroxides. The type is independent of the nature of the enclosed liquid and of the gel skeleton. The relative contraction which occurs when the liquid is completely removed from the pores of a gel has been determined in several cases. Experiments with hardened gelatin gels indicate that the canals are from 30 to 100 times smaller than was supposed by Bütschli in his honeycomb theory of gels. Canals of 700—800 $\mu\mu$ diameter would have no appreciable effect on the vapour pressure, and the discontinuities observed microscopically must be regarded as subsidiary to the main structure of the gel. The dehydration and hydration curves of coconut charcoal exhibit two hysteresis areas, indicating systems of pores of different dimensions.

Permutite, according to its behaviour with benzene, has a structure comparable with that of old solid silica gels, and its largest pores are relatively coarse (20 $\mu\mu$ and more in diameter). Hydrophane behaves as a very old silica gel, artificial gels of increasing age giving curves which tend to approach those of hydrophane as a limiting conditon. C. H. D.

A New Method of Preparing Colloids. JNANENDRA CHANDRA GHOSH (*Rep. Indian Assoc. Sci.*, 1915, 87—89).—If a dilute solution of a salt of a heavy metal is electrolysed with a large platinum anode and a platinum point cathode, and electric oscillations are impressed on the circuit, the metal is not deposited on the cathode, but remains suspended in the form of a colloidal solution. Silver and mercury sols have been obtained in this way, and in the case of silver it has been found that the quantity of the sol is proportional to the total quantity of electricity furnished by the source of the direct current.

H. M. D.

Mechanism of the Precipitation Process. H. R. KRUYT and JAC. VAN DER SPEK (*Chem. Weekblad*, 1917, **14**, 950—953).—A theoretical paper, discussing the influence of the nature of the ions and the concentration on the precipitation of colloidal solutions.

A. J. W.

Physico-chemical Analysis of Colloidal Ferric Hydroxide. WOLFGANG PAULI and JOHANN MATULA (*Kolloid Zeitsch.*, 1917, **21**, 49—63).—An attempt has been made to ascertain the constitution of hydrosols and in particular to trace the origin of the electrical charge of the colloidal particles of ferric hydroxide by potential difference and conductivity measurements and observations on the coagulation produced by the addition of electrolytes.

The data suggest that ferric hydroxide sol is to be regarded as a complex salt, the anion of which is identical with that in the ferric salt used in the preparation of the sol. From the electrometric data and chlorine estimations for a sol prepared from ferric chloride, it would seem that the ionisation of the complex chloride corresponds

with that of a moderately strong electrolyte. By the addition of other electrolytes having an ion in common, changes are brought about which can be readily interpreted as mass action effects. The coagulating power of added electrolytes appears also to be determined by the solubility product for the combination of the colloid ion and the anion of the coagulant. According to this view, inorganic colloids show a close resemblance in their behaviour to that of typical electrolytes.

The question of the structure of the complex colloid ion is not nearly so clearly indicated by the experiments described, but the facts suggest that the sol may be represented by the formula $x\mathrm{Fe(OH)_3}\,.\,y\mathrm{Fe}^{\cdot\cdot\cdot}3y\mathrm{Cl}'$. This formula accords with the fact that chlorine ions only are removable by dialysis. The cations accompanying the chlorine ions are hydrogen ions, and since the electrometric measurements indicate that such sols are neutral, it would seem that the corresponding hydroxyl ions react with the ferric ions to produce ferric hydroxide, thereby leading to an increase in the value of x. The sol particles thus increase in size and become more susceptible to the action of coagulants. Changes in viscosity which accompany the ageing of colloids may possibly be explained in a similar manner.

The theory put forward is discussed in relation to other hypotheses which have been advanced to account for the characteristic properties of colloids and also to the micellary theory of colloid structures. H. M. D.

The Molecular Condition of Acetic Acid in Boiling Benzene and in the Saturated Vapour from the Solution. ERNST BECKMANN, OTTO LIESCHE, and WERNER GABEL (*Zeitsch. physikal. Chem.*, 1917, **92**, 421—432).—When an associating volatile substance like acetic acid is dissolved in a non-associating solvent like benzene, the complete statement of the equilibrium conditions at the boiling point of the solution involves a knowledge of the dissociation equilibrium in the vapour and liquid phases and of the distribution of the two kinds of molecules between the vapour and liquid phases.

Measurements have been made of the change produced in the boiling point of benzene by the addition of varying quantities of acetic acid and of the composition of the co-existing liquid and vapour phases.

Denoting by p_1 and p_2 the partial pressures of the single and double molecules of acetic acid in the vapour, and by P_1 and P_2 the osmotic pressures in the liquid solution, then the equilibrium relations may be expressed by $p_2/p_1^2=\chi$, $P_2/P_1^2=k$, $P_1/p_1=l_1$, and $P_2/p_2=l_2$, from which $\chi l_2/kl_1^2=1$.

As the concentration of acetic acid increases, the difference, Δ, between the boiling point of the solution and that of the solvent, which is at first negative, increases to a maximum, then decreases, and finally becomes positive. For the solution for which $\Delta=0$, the value of g (acetic acid per 100 grams of liquid benzene) is 6·275 and

the value of γ (acetic acid per 100 grams of benzene vapour) is 4·796. From these data and $\chi = 20{\cdot}69$, the following values of the equilibrium coefficients are derived: $k = 1{\cdot}350$, $l_1 = 98{\cdot}64$, and $l_2 = 634{\cdot}9$.

If n is the number of molecules of acetic acid in the liquid and ν the corresponding number for the vapour, then the change in the boiling point is given by $\Delta = K(n - \nu)$, in which K is the normal molecular elevation of the boiling point. The values of Δ, calculated from this equation by the aid of the above equilibrium constants, are found to be in satisfactory agreement with the observed values. H. M. D.

Systems of many Components. W. EITEL (*Zeitsch. anorg. Chem.*, 1917, **100**, 95—142).—When the number of components in a system is greater than four, the ordinary geometrical representation of the phase relationships is impossible. Such systems may be represented by an application of polydimensional geometry (compare Boeke, this vol., ii, 178). An N-component system is represented by a 'polytope,' T_N, of $N-1$ dimensions, and the number of binary, ternary, and higher systems may be calculated in each case. Thus a 5-component system includes 10 binary, 10 ternary, and 5 quaternary systems. Such polytopes may be projected on to a plane, and the polygons thus obtained have $N-1$ sides, the remaining point being placed at the centre. Details of the geometrical construction are given, and the methods of projection are described, being worked out in detail for the case of a 5-component system, in which all the components separate as pure solid phases. A few special cases of solid solution are also examined. C. H. D.

The System Aniline-Hexane. DONALD B. KEYES and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1917, **39**, 2126—2137).—Normal liquids are with few exceptions miscible in all proportions, and as a result of the examination of 500 pairs, the only liquids of this type found to give two liquid systems were aniline and pentane or hexane, and also naphthylamine and pentane or hexane.

With the view of finding an explanation for the deviations from Raoult's law, the physical properties of mixtures of aniline and hexane have been examined. These properties include the vapour pressure, heat of mixing, surface tension, change of volume on mixing, compressibility, and the mutual solubility in its dependence on the temperature.

The vapour pressures show a strong positive deviation from the requirements of Raoult's law, the deviations being much greater than those which follow from the assumption that the aniline is associated to form double molecules or molecules of still greater complexity. The formation of mixtures is accompanied by heat absorption, by expansion for mixtures rich in hexane, and by contraction for mixtures rich in aniline. The surface tension of the mixtures is less than that given by the mixture rule, whilst the compressibility for mixtures rich in hexane is greater, and for mixtures

rich in aniline less than that calculated by the mixture rule. The theoretical significance of the observations is discussed briefly.

H. M. D.

Piezo-chemical Studies. XIV. Influence of Pressure on the Velocity of Reaction in Condensed Systems. III. ERNST COHEN and A. M. VALETON (*Zeitsch. physikal. Chem.*, 1917, **92**, 433—470. Compare A., 1915, ii, 246).—The apparatus employed by Cohen and de Boer in the investigation of the influence of pressure on the rate of inversion of sucrose in presence of hydrochloric acid (A., 1913, ii, 687) has been improved in detail and used in further experiments in which acetic acid was used as catalyst at 25°, 35°, and 45° under pressures reaching up to 1500 atmospheres.

The results obtained show that the velocity-coefficient increases as the applied pressure increases, but that the rate of increase is much smaller at pressures above about 1000 atmospheres. When the numbers are corrected for the change in concentration due to the compressibility of the solutions, it is found that the velocity-coefficient is independent of the pressure at pressures above 1000 atmospheres.

On comparing the results with those obtained previously by Stern, considerable discrepancies are found.

H. M. D.

Contact Catalysis. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 573—602).—The phenomena of contact catalysis are discussed, with particular reference to the theories which have been advanced in explanation of these effects. The author arrives at the conclusion that contact catalysis depends on adsorption and that the catalytic effect may in some cases be explained entirely on the basis of the increased surface concentration. Solids which act as catalysts may be considered as equivalent to a solvent, and hence may cause a displacement of the equilibrium. The displacement is favourable to the system which is more strongly adsorbed.

As a consequence of selective adsorption, the products obtained may vary with the nature of the solid catalyst.

H. M. D.

The Conception of the Chemical Element. K. FAJANS (*Jahrb. Radioaktiv. Elektronik*, 1917, **14**, 314—352).—A long discussion of how the accepted facts in regard to isotopic elements may be reconciled with the current conception of the chemical element originating with Boyle is summarised as follows. It is not justifiable to consider iostopic elements as the same element and isotopes as different kinds of the same element. The common methods of chemical analysis only fail to distinguish between isotopes if they are qualitative. The difference in equivalent shows that isotopes cannot be considered as the same element. It is more convenient to regard isotopes as different elements and to create a new conception "elementary type" to include them. Although the accepted elements may themselves be mixtures of isotopes, until this is demonstrated they should be called elements—an element

being considered a substance not yet, rather than one that cannot be, separated. Those, not yet separated into their constituents, but which we can with certainty conclude are mixtures, are not to be considered elements. The definition of an element proposed is "a substance that has not been separated into simpler constituents and is not known to be a mixture of other substances." According to this definition, there are 92 elementary types or pleiads. Of 77 types only one element, of 6 types no element, and of the remaining 9 types several (two to seven) elements are known, making the total number of elements, or kinds of atoms, known to-day as 117.

F. S.

Distilling Head. ORLO STEARNS (*J. Ind. Eng. Chem.*, 1917, **9**, 972—973).—The bulb forming the essential part of the apparatus is "heart-shaped" in section; the tube leading to the condenser leaves the depression at the top of the bulb, and is inclined upwards at an angle of 110° from the vertical before it is bent downwards to join the top of the condenser. This tube diminishes in diameter from 15 mm., where it leaves the bulb, to 7 mm. at a distance of 4 cm. above the bulb. The tube leading from the distillation flask enters the lower part of the bulb and extends into the latter, this part of the tube being bent over so that the end points downwards inside the bulb. A small hole is provided at the bottom of the portion of the tube which is inside the bulb so that liquid may return to the flask. W. P. S.

Mercury Vapour Pumps for Operating against High Pressures. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1917, **39**, 2183—2186).—The pump described has been designed with the object of avoiding the necessity for the use of an auxiliary pump giving a relatively high vacuum.

It consists of two mercury pumps operating in series, the initial reduction in pressure being attained by the use of an ordinary water-jet pump. The evacuation is effected by a rapid stream of mercury vapour which passes through a suitable nozzle, each pump being provided with a boiling tube and water-cooled condenser. The first of the two mercury pumps operates against a back pressure as high as 40 mm. and gives a vacuum of less than 1 mm. The second operates against back pressures up to 7 or 8 mm. and gives a vacuum as good as that which is attainable by other pumps of this type. H. M. D.

New Shaking Apparatus and their Application. H. THOMS (*Ber.*, 1917, **50**, 1242—1244).—A cage for a bottle, or a plate to which tubes can be clamped, is fitted into a framework so that it can be rotated about its axis (compare this vol., ii, 561).

J. C. W.

The Nomon—A Calculating Device for Chemists. HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1917, **39**, 2137—2144).—The

nomon, or nomographic reckoner, is a calculating chart with a degree of precision from five to ten times that of an ordinary 10-in. slide rule, by means of which it is possible to multiply, divide, square, cube, and to extract square and cube roots with an average error of about one unit in the fourth place. Its employment in chemical practice is illustrated by examples. H. M. D.

Lecture Experiment :—Preparation of Sodium. SIEGFRIED WIECHOWSKI (*Chem. Zeit.*, 1917, **41**, 739).—A stick of sodium hydroxide is grooved in the direction of its length and placed in a shallow glass dish. A knitting-needle is brought into contact with the sodium hydroxide at each end of the narrow trough, pressure being applied so as to make the contact as intimate as possible. After ten to fifteen minutes, the sodium hydroxide has absorbed sufficient moisture to make the system a conductor, and if the needles are connected through a suitable resistance with a 110 or 220 volt circuit, the current passes and metallic sodium is deposited at the cathode. To prevent oxidation, the rod of sodium hydroxide may be covered with a layer of liquid paraffin. H. M. D.

Inorganic Chemistry.

An Improved Hydrogen Chloride Generator. O. R. Sweeney (*J. Amer. Chem. Soc.*, 1917, **39**, 2186—2188).—The generator consists of a separating funnel which is half filled with strong sulphuric acid. This is fitted with a two-holed rubber stopper. Through one hole is passed a piece of capillary tubing about 40 cm. in length, the upper end of which is sealed on to a dropping funnel containing hydrochloric acid (D 1·18). When the hydrochloric acid is allowed to flow into the sulphuric acid, hydrogen chloride is given off in a steady stream, the rate of generation of the gas being controlled by the tap on the dropping funnel. The spent sulphuric acid, which is readily discharged, contains very little hydrogen chloride, and may be used for many laboratory operations. H. M. D.

Recovery of Perchlorate Residues obtained in Potassium Estimations. A. Vürtheim (*Chem. Weekblad*, 1917, **14**, 986—988).—The perchlorate residues are converted into potassium perchlorate, from which the perchloric acid is liberated by distillation under reduced pressure with sulphuric acid. The acid evolved is absorbed by means of water. A. J. W.

Reduction of Selenic Acid. E. B. Benger (*J. Amer. Chem. Soc.*, 1917, **39**, 2171—2179).—Contrary to Mitscherlich's statement,

selenic acid is reduced by hydrogen sulphide. The rate of reaction increases with the temperature and with the concentration of the acid. The complete reaction may be represented by the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but the mechanism is more complicated than this equation suggests.

Selenic acid is also reduced by sulphur dioxide, the reaction taking place in two stages represented by the equations $H_2SeO_4 + SO_2 = H_2SO_4 + SeO_2$, $SeO_2 + 2H_2O + 2SO_2 = 2H_2SO_4 + Se$.

The reducing action of sulphur and selenium has also been examined. In the anhydrous condition, selenic acid is reduced by sulphur at about 60°; in aqueous solution, the reaction requires a higher temperature. Selenium reduces the acid in aqueous solution at the ordinary temperature. H. M. D.

Reduction of Telluric Acid. E. B. BENGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2179—2183).—Aqueous solutions of telluric acid of all concentrations are slowly reduced by hydrogen sulphide and by sulphur dioxide. In 30% solution, the acid is reduced by sulphur, selenium, and tellurium when heated in a sealed tube at 110°.

By comparison with selenic acid, telluric acid is not so easily reduced. Although this is not in accordance with the behaviour expected according to the periodic grouping of the elements of the sulphur group, it is in harmony with the thermochemical data.

H. M. D.

The Distillation of Mixtures of Nitric and Sulphuric Acids. PAUL PASCAL (*Compt. rend.*, 1917, **165**, 589—591).—A study of the ternary mixture water–sulphuric acid–nitric acid. Two diagrams are given, one showing the surface of the boiling points under normal pressure, the second showing the variations in the concentrations of nitric acid in the vapours emitted on distillation.

W. G.

The Effect of the Partial Pressure of Oxygen on Combustion. H. C. DOLLWIG, A. C. KOLLS, and A. S. LOEVENHART (*J. Amer. Chem. Soc.*, 1917, **39**, 2224—2231).—In mixtures of oxygen and nitrogen at atmospheric pressure the flame of a paraffin or a tallow candle, and of an ethyl alcohol (99·8%) lamp, with an asbestos wick are extinguished at the following partial pressures of oxygen: 116 mm. of mercury for the candle and 112·7 mm. for the alcohol. On rapidly evacuating a chamber filled with air, the flames of the candle and the lamp are extinguished at the following partial pressures of oxygen: 19 mm. of mercury for the candle and 27 mm. for the alcohol. W. G.

The Bunsen Flame under Diminished Pressure. L. UBBELOHDE and R. ANWANDTER (*J. Gasbeleucht.*, 1917, **60**, 225—232, 242—246, 268—273; from *Chem. Zentr.*, 1917, ii, 271—272).—The chemical actions which usually occur in the gas flame may be represented by the equations: (1) $CO + H_2O \rightleftharpoons CO_2 + H_2$; (2) $2CO + O_2 \rightleftharpoons 2CO_2$; (3) $2H_2O + O_2 \rightleftharpoons 2H_2O$. Diminution of pressure disturbs the equilibria in (2) and (3) in such a manner that the dissociation of carbon dioxide and water vapour is increased.

It might therefore be expected that the rate of reaction would be so diminished by decreasing the pressure (in consequence of the slow combustion and the increased dissociation and resulting depression of temperature) that a closer study of the chemical processes would be rendered possible. For details of apparatus, the original paper must be consulted.

The authors are led to the following conclusions. The maximum velocity of inflammation of theoretical mixtures of carbon monoxide and air increases from 42 cm. per second at 760 mm. to 60 cm. per second at about 300 mm.; at lower pressures the maximum sinks, and has the value 47 cm. per second at 173 mm. With decreasing pressure, equilibrium becomes less completely established at 1 mm. above the inner cone; at 760 mm. the theoretical mixture of carbon monoxide and air is so far burnt as to contain 26% CO_2, whilst at 162 mm. only about 5% CO_2 is present. Consequently, the calorimetric temperature of the flame is 2020° at 760 mm. and 730° at 162 mm. The probable temperature is about 300° below the calorimetric at 760 mm.; with decreasing pressure the difference probably becomes less pronounced until, at about 140 mm., the temperatures are identical. Below 140 mm., combustion is so incomplete that a flame can no longer be obtained with the ordinary Bunsen burner. With increasing previous heating of the gases, combustion becomes more difficult, and consequently also the attainment of equilibrium. Delayed combustion above the inner cone becomes more pronounced with decreasing pressure. At low pressures, the greater portion of the gases undergoes combustion above the visible portion of the inner cone (above the luminous zone). The maximum temperature in flames burning under low pressure lies about 5—7 mm. above the top of the inner cone. At a pressure of 400 mm. the luminous zone begins to show measurable thickness (at 400 mm., 0·3 mm.; at 200 mm., about 1·6 mm.; at 145 mm., about 2·7 mm.). It has not been experimentally proved whether this phenomenon is caused by an actual thickening of the zone or by oscillation of an extremely narrow zone. Under ordinary conditions, the theoretical mixture of carbon monoxide and air is only burnt to about 26% CO_2 in the inner cone. H. W.

Recovery of Potassium and Aluminium Salts from Mineral Silicates. J. C. W. Frazer, W. W. Holland, and E. Miller (*J. Ind. Eng. Chem.*, 1917, **9**, 935—936).—Finely ground felspar is mixed with four-fifths of its weight of potassium hydroxide or an equivalent quantity of sodium hydroxide, and a small quantity of water, the mixture is dried, and heated for one hour at 300°. The mixture is then treated with water and the insoluble portion is separated by filtration. This insoluble portion has the composition $KAlSi_2O_6$; the alkali used passes into the filtrate and may be recovered. The insoluble compound is then treated with a quantity of hydrochloric acid equivalent to the potassium content; potassium chloride is formed, whilst the aluminium silicate remains insoluble. The latter is readily decomposed by sulphuric acid, yielding aluminium sulphate. W. P. S.

Pure Sodium Chloride. VERNON C. SHIPPER (*Chem. News*, 1917, **116**, 213—214).—Estimations have been made of the quantity of potassium chloride in various samples of sodium chloride purified by fourfold recrystallisation from water. The results indicate that the potassium chloride can be eliminated by recrystallising the sodium chloride a sufficient number of times.

H. M. D.

Studies of the Carbonates. III. Lithium, Calcium, and Magnesium Carbonates. CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD (T., 1917, **111**, 994—1001. Compare this vol., ii, 196).—In continuation of the investigation of the constitution of solutions of the alkali metal carbonates, experiments have been made with lithium, calcium, and magnesium carbonates.

The solubility of lithium carbonate in carbonic acid solutions of varying concentration indicates that ionisation takes place in two stages, the degree of ionisation being the same as for sodium carbonate.

The ionic solubility product of calcium is $[Ca^{\cdot\cdot}]\cdot[CO_3'']=71{\cdot}9\times10^{-10}$, which is lower than the values previously recorded. This gives $[Ca^{\cdot\cdot}]=14{\cdot}6\times10^{-5}$ for a saturated solution of calcium carbonate in pure water at 25°. In this solution, the carbonate is hydrolysed to the extent of 66%.

Crystalline magnesium carbonate ($MgCO_3,3H_2O$) is decomposed by water, and equilibrium conditions have not been obtained. The reaction approximates to

$$5MgCO_3+2H_2O=3MgCO_3,Mg(OH)_2+Mg(HCO_3)_2.$$

In presence of sufficient carbonic acid, the carbonate is stable, and from Engel's data at 12·5°, the ionic solubility product

$$[Mg^{\cdot\cdot}]\cdot[CO_3'']=141\times10^{-6}.$$

H. M. D.

Silver Electro-colloids. G. REBIÈRE (*Bull. Sci. Pharmacol.*, 1917, **24**, 193—204; from *Chem. Zentr.*, 1917, ii, 276—277).—Electro-hydrosols of silver are obtained by passing a suitable current through silver electrodes immersed in water contained in a hard glass beaker cooled in ice-water. The electrodes are placed 1 cm. below the surface; 110—120 volts and 5—10 amperes should be used. When the current is passed, a smoky arc soon appears between the electrodes, which must be maintained by suitable regulation. The separation of colloidal silver is accompanied by a reverse current. In general, the method is similar to that used by Svedberg in the preparation of solutions of metallic colloids in organic media, except that water is here employed. The silver hydrosols appear cloudy by reflected, clear by transmitted light, and are variously coloured (grey, yellow, violet, green, and red), depending on the size of the particles and the nature of the intercorpuscular liquid. The concentration of the metal is of secondary importance.

For the determination of the chemical composition of the electro-

hydrosols, a separation of the corpuscles and intercorpuscular liquid is essential, which may be effected by several methods (coagulation by electrolytes, ultra-filtration, centrifuging, coagulation, dissociation, etc.). Quantitative results can only be obtained by precipitation with very dilute electrolytes and subsequent centrifuging. Barium nitrate is added to the hydrosol in such quantity that the concentration of the salt is approximately $1/5000N$; after a few minutes, the mixture is centrifuged at a rate of at least 9000 revolutions per minute. In this manner, the components are obtained in the same ratio as that in which they exist in equilibrium in the electro-hydrosol. Silver is estimated by the cyanide method. The silver hydrosols appear deeper brown by transmitted light in proportions as they contain less silver; with increasing silver content, the colour becomes more markedly green. The electrical conductivity increases with increasing silver content. The purity is expressed by the formula $100(Ag\delta/Agt)$. The colloidal silver precipitated from the hydrosols is a dull, anhydrous, black powder which sometimes has a yellow lustre and shines when rubbed. It absorbs carbon dioxide from the air, dissolves readily in nitric acid with evolution of nitrous fumes, yields metallic silver and chlorine with hydrochloric acid, and is decomposed at a bright red heat into silver and oxygen. It therefore appears to be a lower oxide of silver containing Ag 96·4—97·98%. The conductivity of the intercorpuscular liquid obtained by ultrafiltration is higher than that of the water used; it is therefore a solution of silver oxide. H. W.

The Oxy-salts of the Alkaline Earth Metal Haloids. Equilibria in Ternary Systems. II. J. MILIKAN (*Zeitsch. physikal. Chem.*, 1917, **92**, 496—510. Compare this vol., ii, 257).—The equilibrium conditions in the ternary systems formed by the alkaline earth chlorides, hydrogen chloride, and water have been examined at 25°.

In the system $CaCl_2$–HCl–H_2O, the solution containing 44·50% $CaCl_2$ and 3·3% HCl is in equilibrium with the solid phases $CaCl_2,6H_2O$ and $CaCl_2,4H_2O$, and the solution containing 28·48% $CaCl_2$ and 21·40% HCl with the solid phases $CaCl_2,4H_2O$ and $CaCl_2,2H_2O$.

In the system $SrCl_2$–HCl–H_2O, the solid phases occurring at 25° are $SrCl_2,6H_2O$ and $SrCl_2,2H_2O$, and these co-exist in equilibrium with a solution containing 2·11% $SrCl_2$ and 27·14% HCl.

For the system $BaCl_2$–HCl–H_2O, the equilibrium data at 30° have been previously published by Schreinemakers (A., 1912, ii, 760). By combining the data for the system salt–acid–water with the data for the system salt–base–water (previous paper, *loc. cit.*), a survey of the equilibrium relations in both alkaline and acid solutions is obtained. H. M. D.

Formation of Tricalcium Aluminate. EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1917, **9**, 943—946. Compare A., 1914, ii, 772).—Tricalcium aluminate seems to be best formed when the

compound $5CaO,3Al_2O_3$ is kept for a long time in contact with lime at a temperature just above the melting point of the eutectic solution of lime (1395°), but below the melting point of the pure compound, $5CaO,3Al_2O_3$ (1455°). The binary system of lime and alumina, containing more than 47·8% CaO, should be regarded as a solution of lime in the compound $5CaO,3Al_2O_3$. Tricalcium aluminate may be considered to be a metastable saturated solid solution of lime in $5CaO,3Al_2O_3$, or as $5CaO,3Al_2O_3$ with 4 mols. of CaO of crystallisation, rather than as a stable phase in the strict sense of the word. W. P. S.

The Refractory Properties of Magnesia. H. Le Chatelier and B. Bogitch (*Compt. rend.*, 1917, **165**, 488—491).—A comparison of some six types of magnesia bricks for furnaces with reference to their resistance to crushing with rise in temperature. The best type, as regards high magnesium oxide content, showed a sudden fall in resistance at between 1500° and 1600°, less pure types showing a similar fall at between 1300° and 1400°. A ferrochrome brick similarly compared showed a rapid loss of solidity at 1100°. W. G.

Theory of the Electrolytic Formation of Lead Tetrachloride. Robert Kremann and Hermann Breymesser (*Monatsh.*, 1917, **38**, 113—120).—The authors have investigated the mechanism of the formation of lead tetrachloride by the electrolytic oxidation of a solution of hydrochloric acid (D 1·18) saturated with lead chloride (Elbs and Nübling, A., 1903, ii, 727). There are two possibilities: (1) the tetrachloride is directly formed on the anode and acts as a depolariser on the carbon electrode, or (2) lead chloride is formed on the anode and this then reacts in the solution with chloride liberated from the carbon electrode. To decide between the two possibilities the authors have determined the decomposition voltage at 0° and 21° of solutions of hydrochloric acid (D 1·18) and of similar solutions saturated with lead chloride. It is found that two breaks occur in each of the current-voltage curves. The first break occurs at 0·83 volt at 0° and 0·87 volt at 21°, and is the same for both solutions. The second occurs for hydrochloric acid alone at 0·99 volt at 0° and 0·95 volt at 21°, whilst for hydrochloric acid saturated with lead chloride the values are 1·04 volts at 0° and 1·00 volt at 21°. From these results it is shown that the formation of lead tetrachloride is a secondary process between the lead chloride and chlorine formed respectively on the lead and carbon anodes, and differs in no way from the chemical method of formation of this substance as described by Friedrich (A., 1893, ii, 415). J. F. S.

The Heterogeneity of Steels. G. Charpy and S. Bonnerot (*Compt. rend.*, 1917, **165**, 536—540).—The authors find that the cupric reagent of Le Chatelier and Lemoine gives much clearer results than the other reagents commonly used for the attack of

steels prior to microscopic examination. They consider that the study of the heterogeneity of steels should be directed to two points, namely, (1) the distribution and relative dimension of the juxtaposed elements, and (2) the difference of quality between these elements. W. G.

Electrolytic Deposition of Alloys and their Metallographic Examination. VII. Experiments on the Cathodic Preparation of Pyrophoric Deposits from Glycerol–Water Solutions of Iron Salts with additions of other Salts, particularly Cerous Chloride. ROBERT KREMANN, RUDOLF SCHADINGER, and RICHARD KROPSCH (*Monatsh.*, 1917, **38**, 91—111. Compare A., 1914, ii, 96, 422, 615, 616).—In a previous paper experiments are described whereby pyrophoric alloys were prepared from solutions of iron salts in the presence of glycerol and magnesium salts. The present paper describes similar experiments in which cerous chloride is substituted for magnesium chloride. The experiments were carried out at various current densities and potential differences. The solutions contained quantities of glycerol amounting to 75% and 50% of the whole solution. The hardness and pyrophoric character of the various deposits were determined in every case. It is shown that the substitution of cerous chloride for magnesium chloride does not increase the pyrophoric character of the deposit. In some cases a comparatively large amount of cerium is deposited along with the iron, but in no case is the amount so large as that contained in the technical pyrophoric cerium alloys. The presence of large amounts of cerium in certain cases is regarded as being due to secondary causes, and not to direct electrolytic deposition. A series of microphotographs of the various cathode deposits described is appended to the paper. J. F. S.

Ferric Oxide and Alumina. FRANCIS H. SCHEETZ (*J. Physical Chem.*, 1917, **21**, 570—572).—The yellow colour in bricks has been shown previously to be due to a yellow modification of anhydrous ferric oxide, which is rendered stable by alumina. In reference to this effect, some experiments have been made, in which solutions containing ferric and aluminium sulphates were precipitated with sodium carbonate, sodium hydroxide, and lime, the washed precipitates being dried and then heated gradually up to 1000°. The precipitates obtained with lime water gave a buff-coloured product provided that the oxide mixture contains less than 8% of ferric oxide. The buff colour is not obtained when sodium carbonate or hydroxide is the precipitant. H. M. D.

The Arrangement of the Atoms in Tungsten. P. DEBYE (*Physikal. Zeitsch.*, 1917, **18**, 483—488).—The *X*-ray method for the investigation of crystal structure, described previously (compare this vol., ii, 437), has been applied in the investigation of samples of powdered tungsten. In spite of the fact that *X*-rays are very strongly absorbed by the metal, it has been found possible to obtain

interference figures, from which it is clear that tungsten crystallises in cubic forms, and that the elementary space lattice is a cube with a centrally situated point, the length of the edge of the cube being $3\cdot18 \times 10^{-8}$ cm. H. M. D.

The Search for Two Unknown Metals (Neomolybdenum and Neotungsten). M. GERBER (*Mon. Sci.*, 1917, [v], **7**, 73—83, 121—127, 169—177, 219—226).—The author claims to have discovered that neither molybdenum nor tungsten is a simple substance, each of these metals being accompanied by closely related, hitherto unrecognised elements, to which the names *neomolybdenum* and *neotungsten* have been given. It is suggested that the two new elements will fill the two unoccupied positions in the periodic table in group VII below manganese, their atomic weights being estimated approximately as: neomolybdenum = 99·9, neotungsten = 188. Chemically, each of the new elements is very closely related to the element with which it is found associated, and spectroscopically is quite indistinguishable therefrom. On this account it is suggested that each new element is a metallic isotope of the element with which it is associated, by analogy with the two forms of lead, which appear to be chemically and spectroscopically identical.

Neomolybdenum was separated from molybdenum by fractional crystallisation of a specimen of ammonium molybdate prepared from molybdenite from Glen Innis, New South Wales. The most soluble fraction, when analysed, gave for the metal an atomic weight = 100 (Mo = 96), and, moreover, the acidic oxide obtained by heating this ammonium salt was far more volatile than ordinary molybdic acid. The properties of neomolybdenum do not agree with those of the nipponium of Ogawa (A., 1908, ii, 952) supposed to be ekamanganese.

From soluble metatungstic acid the author has prepared the ammonium *iso*tungstate described by Laurent, the existence of which has been since denied or overlooked. In the *iso*tungstic acid prepared from this, the metal had an atomic weight = 186·5 to 187 (W = 184). This *iso*tungstic acid, it is supposed, contains neotungsten. A long historical account of the tungstates is given.

E. H. R.

Mineralogical Chemistry.

Minasragrite, a Hydrous Sulphate of Vanadium. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1917, **7**, 501—503).—This mineral occurs abundantly at Minasragra, Peru, as a blue efflorescence on patronite, of which it is an alteration product. It is also being formed at the present time on museum specimens of patronite. On the specimen examined are the primary

minerals patronite, quisqueite, and bravoite, and the secondary minerals minasragrite, melanterite, morenosite, and gypsum. The mineral is probably monoclinic or triclinic, and has refractive indices $\alpha = 1·515$, $\beta = 1·525$, $\gamma = 1·545$. It is readily soluble in cold water; analysis of impure material gave:

V_2O_4.	FeO.	NiO.	CaO.	SO_3.	Insol. in water.	H_2O (diff.).
5·29	0·97	1·92	0·46	10·92	66·16	[14·28]

Deducting iron, nickel, and calcium as melanterite, morenosite, and gypsum respectively, the figures for the vanadium sulphate become: V_2O_4, 24·64; SO_3, 33·17; H_2O, 42·19%, corresponding with the formula $V_2O_4,3SO_3,16H_2O$, which is interpreted as a hydrated acid vanadyl sulphate, $(V_2O_2)H_2(SO_4)_3,15H_2O$. L. J. S.

Measurements of the Radioactivity of Meteorites. TERENCE T. QUIRKE and LEO FINKELSTEIN (*Amer. J. Sci.*, 1917, [iv], **44**, 237—242).—The radium content of twenty-two meteorites not previously analysed was determined. The method of preparation consisted in dissolving the metallic part of the mineral in hydrochloric and nitric acid, and the undissolved part by fusion, separating the radium from the solution obtained by barium sulphate. The latter was fused with potassium-hydrogen sulphate in a test-tube, which was sealed. After the emanation had accumulated, the contents of the tube were again fused and air drawn through into the emanation electroscope. The results showed that the average stony meteorite contains less than a quarter of the radium in an average granite—$7·6 \times 10^{-13}$ gram of radium per gram of meteorite for an average of seventeen—and that the metallic meteorites are almost free from radium. The meteorites examined included aërolites, chladnite, eukrites, chondrites, siderolites, iron meteorites, octahedrites, and hexahedrite. F. S.

Analytical Chemistry.

A Universal Gas-Volumeter. HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1917, **39**, 2145—2151).—A direct reading gas-measuring apparatus is described, in which the volume of the gas collected is not only reduced mechanically to standard conditions, but converted automatically into the percentage of any desired constituent, no matter what the nature of the substance or weight of the sample submitted to analysis. H. M. D.

Use of Textile Fibres in Microscopic Qualitative Chemical Analysis. E. M. CHAMOT and H. I. COLE (*J. Ind. Eng. Chem.*, 1917, **9**, 969—971).—Silk fibres, previously treated with

10% sodium hydroxide solution for two hours at the ordinary temperature and then washed, are dyed with concentrated litmus solution, washed, treated with very dilute acetic acid solution or sodium hydroxide solution, and again washed. Fibres thus prepared form very sensitive indicators for the detection of acids or alkalis in minute drops of solution. In testing a drop of solution the fibre is so placed that a part of it is not moistened by the solution, and this part serves for comparison when the drop is observed under the microscope. A $N/4500$-solution of a mineral acid gives a distinct reaction with the fibres, but the reaction with alkalis is not quite so sensitive. The litmus used in preparing the fibres must be purified. Fibres dyed with Congo-red are useless for differentiating organic acids from mineral acids. W. P. S.

Influence of Added Substances on the End-point in the Iodometric Titration of Hydrogen Sulphide. ALFRED R. JAYSON and RALPH E. OESPER (*J. Ind. Eng. Chem.*, 1917, **9**, 975—977).—The red coloration which appears during the titration of hydrogen sulphide with iodine in acid solution is possibly due to acceleration of the hydrolysis of the starch to erythrodextrin under the conditions of the titration. This hydrolysis occurs at the point at which iodine and hydrogen sulphide react, and, although at ordinary concentrations iodine reacts with hydrogen sulphide and combines with starch in preference to erythrodextrin, at high local concentrations erythrodextrin iodide may also be formed. At the end of the titration, the mixture of red erythrodextrin iodide and blue starch iodide gives a purple coloration which changes to blue as the former compound decomposes. The addition of various salts (sodium chloride, calcium chloride, magnesium sulphate, etc.) does not make the end-point more definite.
W. P. S.

Estimation of Sulphur Dioxide [in Gases and Air]. O. R. SWEENEY, HARRY E. OUTCAULT, and JAMES R. WITHROW (*J. Ind. Eng. Chem.*, 1917, **9**, 949—950).—Oxidation with permanganate is recommended, since permanganate solution is more stable than is iodine solution. To ensure complete oxidation, the permanganate must always be present in excess. About 475 c.c. of water, 30 c.c. of $2N$-sulphuric acid, and 10 c.c. of $N/200$-permanganate solution are placed in a stoppered bottle and about one-half of this mixture is transferred to another bottle; a small quantity of sulphurous acid is added to one portion so as nearly to destroy the pink colour, and permanganate solution is then added until the colour is equal to that of the solution in the other bottle; the solutions are again mixed and divided into two portions, one being reserved as a standard. (These operations are necessary owing to the fact that the colour obtained on re-titrating a mixture of sulphurous acid and permanganate is slightly different in tint from that of permanganate alone.) An excess of permanganate is then introduced into one of the bottles, this bottle is connected

with the reservoir containing the sample of gas, the latter and the solution are mixed, and permanganate is then added until the coloration is equal to that of the comparison bottle. The quantity of permanganate solution used in these later operations is equivalent to the amount of sulphur dioxide present. W. P. S.

Estimation of Nitrogen by Kjeldahl's Method. OTTO NOLTE (*Zeitsch. anal. Chem.*, 1917, **56**, 391—393. Compare A., 1916, ii, 146).—In the case of caffeine and uric acid, the digestion with sulphuric acid is accelerated when a current of sulphur dioxide is passed through the mixture, but with tetramethylammonium hydrobromide, the decomposition is still incomplete. The addition of oxalic acid also favours the conversion of caffeine and uric acid into ammonia. W. P. S.

The Estimation of Nitrogen in Urine. MALTE LJUNGDAHL (*Biochem. Zeitsch.*, 1917, **83**, 115—119).—A modification of Kjeldahl's method adapted to small quantities of substance (for example, 1 c.c. of urine), in which the apparatus described by the author for the estimation of acetone (this vol., ii, 584) is employed for distilling off the ammonia. S. B. S.

Estimation of Ammonia in Soils. F. MÜNTER (*Landw. Versuchs-Stat.*, 1917, **90**, 147—189).—See this vol., i, 722).

A Method of Estimating Ammoniacal Nitrogen with Formaldehyde. G. H. C. VAN BERS (*Chem. Weekblad*, 1917, **14**, 968—975).—Formaldehyde reacts with ammonium salts in presence of excess of sodium hydroxide in accordance with the equation $6CH_2O + 2(NH_4)_2SO_4 + 4NaOH = C_6H_{12}N_4 + 2Na_2SO_4 + 10H_2O$. Titration of the excess of alkali furnishes the data required for calculating the percentage of ammonia, phenolphthalein being employed as indicator. Without the excess of alkali, free sulphuric acid is formed, but titration of the acid with alkali gives unsatisfactory results, owing to the end-point of the reaction being indefinite. A. J. W.

Some Factors influencing the Estimation of Nitric Nitrogen in the Soil. J. E. GREAVES and C. T. HIRST (*Soil Sci.*, 1917, **4**, 179—205).—The following procedure is recommended for the estimation of nitrate nitrogen in soil. One hundred grams of the soil are shaken with 500 c.c. of water for five minutes, the solution being clarified either (1) by the addition of 2 grams of potassium alum with the soil, or (2) by filtering through a Chamberland-Pasteur filter, or (3) by centrifuging. If the estimation cannot be proceeded with at once, using methods (2) or (3), 0·5 c.c. of chloroform should be added to the solution. One hundred c.c. of the clear liquid is evaporated with 2 c.c. of strong aqueous sodium hydroxide down to 25 c.c., or, if carbamide is present, to dryness. The liquid is then diluted with 50 c.c. of

water and reduced by Ulsch's method (compare A., 1891, 617, 960), using 5 grams of iron reduced by hydrogen and 30 c.c. of sulphuric acid (D 1·35), the estimation being completed in the usual manner. Provided that the soil is finely powdered, the five minutes' shaking is sufficient, and the proportion of soil to water may vary from 1:5 to 1:25. The chlorides, sulphates, or carbonates of sodium, potassium, calcium, magnesium, manganese, or iron do not interfere with Ulsch's method. W. G.

The Estimation of Soil Phosphorus. CLAYTON O. ROST (*Soil Sci.*, 1917, **4**, 295—311).—A comparison of six different methods for the estimation of the total phosphorus in a soil. The author has modified Washington's method for the estimation of phosphorus in rocks (compare "Manual of Chemical Analysis of Rocks," 1910) to make it equally satisfactory for soils. The modification consists in an ignition at a dull red heat prior to the treatment with hydrofluoric and nitric acids, and later taking up the phosphoric acid with nitric acid, and drying the residue in an air-bath at 110°. The amount of titanium oxide found in soils is too low to interfere with the precipitation of the phosphorus. W. G.

Estimation of Arsenic. III. Application to Iron Arsenic Pills. F. LEHMANN (*Arch. Pharm.*, 1917, **255**, 305—307).—The simplified method of estimating arsenic in animal material previously described (compare Ruff and Lehmann, A., 1912, ii, 866; Lehrmann, A., 1913, ii, 242) is now found to be applicable to vegetable material if the distillate containing the arsenic trichloride is collected, not in a solution of sodium hydrogen carbonate, but in 25% nitric acid; this solution is evaporated to dryness (whereby the volatile fission products of the organic matter which combine with iodine are oxidised), the residue is dissolved in a little alkali, and the arsenic acid in the filtered solution is estimated as usual after the addition of potassium iodide and sulphuric acid.

The application of the method to the estimation of the arsenic in iron arsenic pills is described in detail. C. S.

Testing Sulphuric Acid used in the Manufacture of Dextrose [for Arsenic]. ANDRÉ KLING (*Ann. Falsif.*, 1917, **10**, 451—453).—The Gutzeit test is recommended for the detection of arsenic in sulphuric acid, and a convenient form of apparatus is described for the purpose. W. P. S.

Arsenical Dextrose. ANDRÉ KLING (*Ann. Falsif.*, 1917, **10**, 438—450).—For the detection and estimation of arsenic in dextrose (commercial glucose), the Marsh, Gutzeit, and diaphanometric (turbidity obtained with sodium hypophosphite in sulphuric acid solution) methods are equally trustworthy. The last method, however, cannot be used if nitrates or nitrites are present. The arsenic in dextrose may be precipitated completely by treating the

dextrose solution with bromine and then adding a small quantity of sodium phosphate and "magnesia mixture" and an excess of ammonia; the precipitate obtained is collected, washed, dissolved in nitric acid, the solution evaporated with the addition of sulphuric acid, and the residue tested in the Marsh apparatus. This procedure may be employed in place of the usual method of destroying the organic matter by heating with sulphuric acid and nitric acid. When arsenical dextrose is used in brewing, a small quantity (about one-tenth) of the arsenic present is "fixed" by the yeast when top fermentation yeast is employed; bottom fermentation yeast "fixes" only traces of the arsenic. W. P. S.

Estimation of Zinc by Schaffner's Method. G. FENNER and RÖTHSCHILD (*Zeitsch. anal. Chem.*, 1917, **56**, 384—390. Compare A., 1916, ii, 578).—The necessity of having exactly the same amounts of zinc in the test solution and in the comparison solution applies only to the older modifications of the method. If hydrogen peroxide, potassium chlorate, or bromine is used to oxidise the iron present, care must be taken to remove the excess of these and certain reduction products before the titration is commenced. W. P. S.

Analysis of White Metal Alloys. Estimation of Lead, Copper, and Antimony. R. HOWDEN (*Chem. News*, 1917, **116**, 235).—For the estimation of lead and copper, the alloy (about 1 gram) is dissolved in a mixture of nitric and hydrochloric acids. Five c.c. of sulphuric acid and about 1 gram of tartaric acid are added to the solution, which is heated until the evolution of fumes ceases. The solution is then diluted and the precipitated lead sulphate filtered off. Sulphur dioxide is then passed into the filtrate, and the copper precipitated as cuprous iodide or as thiocyanate. The precipitate is dissolved in dilute nitric acid, and the copper estimated by the addition of potassium iodide and titration with sodium thiosulphate.

To estimate antimony, the alloy is dissolved in hydrochloric acid with the aid of potassium chlorate. Stannous chloride solution is added drop by drop until the yellow colour due to the copper is bleached, and the solution is then diluted and the copper reoxidised by passing air through the liquid. The antimony in the solution is then titrated by means of a standard solution of potassium bromate, the end-point being indicated by the addition of a little methyl-orange, which is bleached when the oxidation of the antimony is complete. H. M. D.

Use of Titanium Trichloride in Analytical Practice. F. MACH and P. LEDERLE (*Landw. Versuchs.-Stat.*, 1917, **90**, 191—224).—The use of titanium trichloride is recommended for various estimations, and when certain necessary precautions are taken, perfectly satisfactory results can be obtained. The authors suggest its use for the estimation of copper in copper sulphate and

in the estimation of sugar by means of Fehling's solution, as well as for the examination of ferrous sulphate and hydrogen peroxide. The results obtained are as accurate as those given by gravimetric methods, and compare favourably with those of the permanganate method for the estimation of hydrogen peroxide. A convenient arrangement of the necessary apparatus is described. H. B. H.

Separation of Aluminium from Iron by means of Ether. SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1917, **9**, 951—953).—The dried, mixed aluminium and ferric chlorides are treated with a small amount of absolute alcohol containing 30% of hydrogen chloride, and the mixture is evaporated until the salts crystallise. The residue is again moistened with acid alcohol containing a trace of water, and ether is added gradually. Hydrated aluminium chloride, of varying composition, is precipitated, whilst the ferric chloride remains in solution. W. P. S.

Estimation of Iron in Glass Sand. JOHN B. FERGUSON (*J. Ind. Eng. Chem.*, 1917, **9**, 941—943).—The sand must be decomposed completely before the iron content can be estimated. Treatment with hydrofluoric acid and sulphuric acid is not sufficient. The insoluble residue should be fused with potassium pyrosulphate, and a subsequent fusion with sodium carbonate is necessary in a few cases. W. P. S.

Estimation of Available Oxygen in Pyrolusite. O. L. BARNEBY (*J. Ind. Eng. Chem.*, 1917, **9**, 961—967. Compare this vol., ii, 274, 390).—The ferrous sulphate and direct iodometric methods are the most trustworthy for the estimation of available oxygen in pyrolusite. The oxalic acid method gives inaccurate results, owing to decomposition of the oxalic acid during the heating required for the solution of the ore; this decomposition is accelerated in sunlight and in the presence of manganese salts. A small quantity of carbon monoxide is evolved from dilute sulphuric acid solutions containing oxalic acid, but oxygen is not liberated when manganese dioxide and oxalic acid react in dilute sulphuric acid solution. W. P. S.

Examination of Light Petroleums and Benzenes. JAROSLAV FORMÁNEK, JOSEF KNOP, and JOSEF KORBER (*Chem. Zeit.*, 1917, **41**, 713—714; 730—731).—The presence of benzene in light petroleums may be detected by shaking a portion of the sample with a small quantity of an aniline colour, such as "Blue BT" or "Violet RT," and filtering the mixture after two hours. If as little as 2% of benzene is present, the liquid will be coloured distinctly. By comparison with standards, this test may be rendered approximately quantitative. The presence of ether, alcohol, carbon disulphide, and chloroform interferes with the test to a certain extent. Tests for the detection of turpentine oil in light petroleum, depending on the absorption of bromine or iodine,

are untrustworthy, since other unsaturated compounds are often present. The freezing point of a sample affords some indication of its composition. Pure benzene freezes at $+5\cdot5°$; a mixture of 25% of benzene and 75% of toluene and xylene at $-10°$ to $-20°$; a mixture of toluene and xylene at $-70°$; and technical xylene at $-115°$. The freezing point of light petroleum varies directly with the boiling point; a fraction boiling at 40° to 60° freezes at $-198°$, whilst a fraction boiling at 200° to 220° freezes at $-93°$.

W. P. S.

Table for the Analysis of Foods containing Sugar. H. Lajoux and L. Ronnet (*Anal. Falsif.*, 1917, **10**, 453—457).—The following table is given as being useful to those engaged in the analysis of substances containing sugars. The solution, Σ, should be prepared from such a quantity of substance that it will contain from 5 to 10 grams of sugar per 100 c.c.; clarification is effected with basic lead acetate and sodium phosphate.

	In 100 c.c. of solution Σ.
Solution Σ: Q grams or V c.c. of sample per 100 c.c.	Sucrose, $S, = \dfrac{95\,D}{176\cdot75/0\cdot56t} = D \times K$.
Solution Σ inverted: Q grams or V c.c. of sample per 110 c.c. Dextrin solution: prepared from 100 c.c. of solution Σ. Fehling solution: 10 c.c. correspond with q gram of invert-sugar.	Reducing sugars, $R, = \dfrac{10{,}000q}{N \times V}$
Solution Σ: Polarisation in 20 cm. tube at $t° = A$. Polarisation of inverted solution in 22 cm. tube at $t° = A'$. $D = A - A'$.	Dextrose, $G, = \dfrac{50A + R(103\cdot4 - 0\cdot56t) - 66\cdot5S}{156\cdot4 - 0\cdot56t}$ If dextrin is present, A is replaced by $A - a$.
	Lævulose, $L, = R - G$.
Solution σ: 10 c.c. of Fehling solution reduced by N c.c.	Dextrose in excess, $g, = G - L$, or lævulose in excess, $l, = L - G$.
Dextrin solution: Polarisation in 20 cm. tube at $t° = a$. Reducing power of saccharified solution, 100/110. 10 c.c. of Fehling solution reduced by n c.c.	Invert-sugar, $I, = 2L$ or $2G$ according to which is the smaller.
	Dextrin, $\Delta, = \dfrac{99 \times q}{n}$

The dextrin solution (if dextrin is present) is obtained by evaporating 100 c.c. of solution Σ to a syrup, adding 3 c.c. of hydrochloric acid and 100 c.c. of 90% alcohol, and collecting the precipitate after three hours. The precipitate is then washed with alcohol, dissolved in hot water, reprecipitated as before, and dissolved in water to make 100 c.c. of solution. Saccharification is effected by boiling

50 c.c. of this solution for three hours with the addition of 0·5 c.c. of hydrochloric acid; after cooling, the solution is neutralised and diluted to 55 c.c. W. P. S.

Schneyer Method for the Estimation of Lactic Acid in Urine. MARY E. MAVER (*J. Biol. Chem.*, 1917, **32**, 71—76).—The modification of Meissner's method for the estimation of lactic acid described by Schneyer (A., 1915, ii, 804) gives results which are too high, owing to the formation of carbon monoxide from hippuric acid and other substances besides lactic acid in the urine. H. W. B.

Estimation of Lactic Acid in Wine by Möslinger's Method. THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 198—207).—Mainly a reply to Baragiola and Schuppli (A., 1914, ii, 752). The barium chloride method as described originally (compare A., 1901, ii, 700; 1902, ii, 180; 1912, ii, 1005) is trustworthy, and, provided that allowance is made for loss of lactic acid during distillation and that the precipitation with alcohol in the proportion of 15:85 is carried out carefully, there is no need to modify the original process. W. P. S.

Estimation of Oxalic Acid in Food. E. ARBENZ (*Mitt. Lebensmittelunters. Hyg.*, **8**, 98—104; from *Chem. Zentr.*, 1917, ii, 320—321).—The oxalic acid content of foods is important in connexion with oxaluria. A table has been drawn up by Esbach for various foods. As doubt has been cast on some of the data, the author has carried out a series of analyses. The usual methods are either cumbersome or insufficiently accurate. The author recommends the following process. The dried material (10—20 grams) is heated under reflux on the water-bath with 15% hydrochloric acid (D 1·074, 150 c.c.), cooled, filtered into a measuring cylinder, and the residue lightly pressed. The clear, dark brown filtrate (120—140 c.c.) is exactly measured and evaporated to dryness. The residue is washed with water (about 20 c.c.) into an Allemann vessel and extracted with ether in a Soxhlet apparatus during twenty-four hours. After removal of the ether, the residue is dissolved in water, treated with ammonia, acidified with acetic acid, and the hot solution is precipitated with an excess of calcium chloride solution. After at least twelve hours, the precipitate is filtered, washed, redissolved in 6 c.c. of hydrochloric acid (15%), and again precipitated, and the process is repeated until the precipitate appears pure under the microscope. It is then ignited and weighed. The following data were thus obtained, the numbers representing grams of oxalic acid in 1000 grams (the figures in brackets are those given by Esbach): black tea, 14·3 (3·7); cocoa, 4·8 (4·5); pepper, 4·5 (3·2); rhubarb, 3·2 (2·4); spinach, 2·9 (3·2); sorrel, 2·7 (3·6); dried fig, 1·2 (1·0); roasted coffee, 0·8 (0·1); roasted chicory, 0·7 (0·7); wild strawberry, 0·6; raspberry, 0·5; bean, 0·45 (0·3); potato, 0·4 (0·4); beetroot, 0·3 (0·4); currant, 0·3;

pear, 0·45 (0·3); bilberry, 0·2; orange, 0·1; asparagus, 0·09 (?); cherry with stone, 0·08; tomato, 0·08 (0·05); grape, 0·08 (?); cabbage, 0·07; cauliflower, 0·06; onion, 0·05; scorzonera, 0·04; endive, 0·03 (0·01); melon, 0·03; mushroom, traces (?); peach, traces (?); meal, traces (0—0·17); lemon, traces (—); celery, traces (0·02); plum, traces (—); apple, traces (traces). Oxalic acid could not be detected in peas, maize meal, rice, or nuts. H. W.

Identification of Picric Acid in a case of Feigned Icterus. Simple Method of Identifying Poison in Blood. Léon Tixier (*Bull. Sci. Pharmacol.*, 1917, **24**, 155—159; from *Chem. Zentr.*, 1917, ii, 249).—The identification of picric acid is easily accomplished in the following manner. Fifteen drops of blood (taken from the finger tip) are mixed with 3 c.c. of sodium chloride solution (9·5%) and allowed to remain in an incubator for twenty-four hours. One to two c.c. of the salt solution are thoroughly agitated with an equal volume of methylene-blue solution (1 : 50,000), 10—15 drops of chloroform are added, and shaking is continued until any precipitate which may have been formed is again dissolved. After subsidence, a noticeable bottle-green to dark green coloration of the chloroform layer shows the presence of picric acid. The reaction is very sensitive and can be effected at a dilution of 1 part in 250,000. H. W.

The Estimation of Acetone. Malte Ljungdahl (*Biochem. Zeitsch.*, 1917, **83**, 103—114).—The actone is distilled off in a current of steam in an apparatus of given dimensions. In the case of urine, 2—5 c.c. are used for analysis, according to the intensity of the Gerhardt reaction. The acetone which distils over is estimated iodometrically. S. B. S.

Colorimetric Estimation of Small Amounts of Aniline. Elias Elvove (*J. Ind. Eng. Chem.*, 1917, **9**, 953—955).—The method depends on the reaction between aniline and a hypochlorite, and is suitable for the estimation of aniline in the atmosphere of places where this substance is used; the aniline is obtained in solution by passing 10 litres of the air through 10 c.c. of very dilute sulphuric acid. According to the indications of a preliminary test, this solution is diluted, if necessary, so that it contains not more than 1 part of aniline in 200,000 parts of solution. Twenty c.c. of the solution are then mixed with 1 c.c. of calcium hypochlorite solution containing about 0·1% of available chlorine, and, after two minutes, 1 c.c. of $N/1$-sodium hydroxide solution is added. After a further ten minutes, the coloration obtained is compared with standards prepared with known amounts of aniline under the same conditions and at the same time. As little as 1 part of aniline in 2,000,000 parts of solution gives a reaction, but in this dilution the coloration obtained is yellow instead of purple.

W. P. S.

INDEX TO PATENTS.

ERRATA.

Vol. LXXXIV (Abstr., 1903).

Part I.

Page	Line	
587	7*	*for* "**87**" *read* "**37**."

Vol. CVI (Abstr., 1914)

Page	Line	
i. 723	27	*for* "$C_{25}H_{29}O_4N_3(OMe)_3$" *read* "$C_{25}H_{29}ON_2(OMe)_3$."

Vol. CVIII (Abstr., 1915).

Page	Line	
i. 820	11*	*for* "nitrite" *read* "nitrile."

Vol. CX (Abstr., 1916).

Page	Line	
i. 135	16	*for* "**86**" *read* "**36**."
i. 422	18	,, "SUCHARD" *read* "SUCHARDA."
i. 820	20*	,, "833" *read* "822."
i. 823	26	*delete the sentence* "Quinhydrones . . . . class" *and read* "Whilst benzoquinhydrone was found to behave differently from dyes or from *meri*quinonoid additive compounds (compare Lifschitz and Jenner, this vol., i, 45; Hantzsch, *ibid.*, 431) its absorption spectrum is by no means typical of the class, which on the contrary is optically similar to *meri*quinonoid salts."
ii. 191	5*	*for* "**Alotrichite**" *read* "**Halotrichite**."
ii. 191	2*	,, "alotrichite" *read* "halotrichite."
ii. 192	13	,, "alotrichites" *read* "halotrichites."
ii. 335	3	,, "molten silicic acid" *read* "silica glass."
ii. 336	4	,, "thermophosphate" *read* "chromophosphate."
ii. 704	12	*insert* **Knorr**, *Angelo*, imino-esters of the thiocyanates A., i, 797.
ii. 719	11*	*for* "**Suchard**" *read* "**Sucharda**."
ii. 741	1	,, "**Suchard**" *read* "**Sucharda**."

Vol. CXII (Abstr., 1917)

Page	Line	
i. 227	1	*for* "6-Nitro-3:4-methylenedioxybenzoic" *read* "6-nitro-3:4-methylenedioxymandelic."
i. 249	6*	,, "SAUREZ" *read* "SUAREZ."
i. 271	17	,, "and preservation of the latter require special precautions" *read* "of the latter has not yet been accomplished."
i. 284	3	,, "quinate" *read* "quininate."
i. 340	9	,, "Bechmann" *read* "Beckmann."
i. 343	14	,, "2:4:6:3′:5′-" *read* "2:4:6:3′:4′-"
i. 343	15*	,, "*α-bromomenzyl*" read "*α-bromobenzyl*."
i. 365	7*	,, "*photophlein*" read "*photophelein*."
i. 366	11, 12, 13	,, "photophlein" *read* "photophelein."
i. 398	17	"*dl*-fenchene" *read* "*Dl*-fenchene." ,, "*d-α*-fenchene" *read* "*Dd*-fenchene."

* From bottom.

Page	Line	
i. 431	13*	*for* “**Semi-barren**” *read* “**Semi-arid.**”
i. 437	13*	,, “beech” *read* “birch.”
i. 466	16	,, “*Fennical*” read “*Fennicae.*”
i. 466	20*	,, “fenchene” *read* “*cyclo*fenchene.”
i. 560	1*	,, “$C_8H_{14}\diagdown\begin{array}{l}CO\\ \mid\\ CO\end{array}$” *read* “$C_8H_{14}\begin{array}{l}\diagup CO\\ \quad\mid\\ \diagdown CO\end{array}$”
i. 572	2	,, “*n*-hexaldehyde” *read* “*n*-heptaldehyde.”
ii. 51	23	,, “J. J. WILLIAMSON” *read* “J. J. WILLAMAN.”
ii. 56	23	,, “PHILIPPI” *read* “FILIPPI.”
ii. 94	4	*after* “NORMAN” *insert* “RAE.”
ii. 179	12	*for* “**700 mm.**” *read* “**760 mm.**”
ii. 324	19	,, “twinned towards the basis” *read* “twinned on the basal plane.”
ii. 324	20	,, whole of line *read* “on the fractured surfaces black with metallic-adamantine lustre; in section, brown and transparent, and exhibiting.”
ii. 324	22	,, “δ” *read* “ϵ.”
ii. 324	23	,, “pleonast” *read* “pleonaste.”
ii. 373	3*	,, “PODZUS” *read* “PODSZUS.”
ii. 569	3*	,, “$\rightleftarrows 2H_2O$” *read* “$\rightleftarrows 2H_2O_2$.”

COLLECTIVE INDEX, 1903—1912 (SUBJECTS).

Page	Col.	Line	
1833	ii	14*	*should read* “euquinine, distinction between quinine and”
2054	ii	31	*for* “1902” *read* “1908”

* From bottom.